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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 5 February 1958, the Chair being taken by F. L. Garton, a member of Council.

The minutes of the previous meeting were confirmed and signed as a correct record. The names of members elected since the previous meeting were also announced.

The Chairman, introducing Dr Agius, who presented the paper, said that he regretted the absence of Mrs Mulvey, who was at that time in the U.S.A.

The following paper was then presented:

THE MECHANISM OF SLUDGE SUSPENSION IN ENGINE OIL *

By P. J. AGIUS † and D. MULVEY †

SUMMARY

The degree of settling of engine sludge dispersed in lubricating oil containing different detergent additives has been determined. The electrophoretic mobility of engine sludge in different hydrocarbons containing the same additives has also been measured. From the results it appears that detergent additives can be divided into two groups:

(1) Those imparting relatively high electrophoretic mobilities to sludge particles kept in suspension with their aid. Such suspensions are coagulated by the addition of additives capable of imparting opposite mobilities to sludge. The ability of the additive or additive mixture to keep sludge in suspension is in general agreement with the magnitude of the resultant mobility of the sludge, irrespective of sense. In the temperature and viscosity range studied, mobility is a function of viscosity but not of temperature.

(2) Those imparting relatively low electrophoretic mobility to sludge suspensions. The additives in this class have all been vinyl ester copolymers. In spite of their low mobilities, their sludge suspensions are very stable and are not easily coagulated by the addition of additives capable of imparting opposing mobilities to the sludge. They are further distinguished by the fact that, in the range studied, the mobilities of their sludge suspensions are dependent on temperature but not on viscosity.

It is concluded that the theories put forward to account for the stability and rate of settling of suspensions which depend on the presence of an electrical double layer at the sludge–liquid interface are generally applicable to additives in the first category, but not to those in the second. In the latter case it is suggested that the stability is due to the greater solvation of the colloidal micelles.

INTRODUCTION

THE formation of sludge in the crankcase oil of gasoline, and to a lesser extent diesel engines, is of considerable practical significance. The presence of an undue quantity of sludge can eventually cause blocking of the small clearances in the oil ways and ducts designed to allow a supply of lubricant to flow over rubbing surfaces. The consequent reduction or stoppage in the lubricant supply will cause heavy wear and ultimate breakdown of the engine. For this reason it has been customary to change the lubricant and flush out the engine at frequent intervals. More recently, by the use of additives, it has been possible to control the formation and deposition of sludge from the lubricant on to the internal parts of the engine so that satisfactory lubrication can be maintained with more protracted oil change periods. Although lubricating oil additives are also used to prevent the formation of varnish and gum on the piston skirt and ring zone, particularly of diesel engines, this paper deals specifically with the suspension of sludge in the crankcase oil of gasoline engines.

This type of sludge is principally formed from fuel combustion residues passing down into the crankcase, and is not caused to any appreciable extent by deterioration products of the lubricating oil itself.[1] Its formation is enhanced by the less volatile components in cracked naphtha, ineffective piston seals, and poor crankcase ventilation. These factors favour the concentration of fuel-derived reactive intermediates in the crankcase which act as precursors to the formation of sludge. It is not surprising therefore that low sump temperatures, favouring as they do crankcase oil dilution, will also promote sludge formation, and that engine operation under these conditions is an important practical problem.

The composition of a sample of sludge is given in Table I. This sample was obtained after 4000 miles of door-to-door delivery van operation using a straight SAE 10 grade lubricant.

It will be seen that it consists mainly of oil, con-

* MS received 6 January 1958.

† Esso Research Ltd.

taining much smaller and similar proportions of inorganic salts and complex organic resins, conveniently distinguished by their solubility in acetone. The virtual absence of elementary carbon is noteworthy.

TABLE I

Composition of Engine Sludge

(SAE 10 grade lubricant—4000 miles of door-to-door delivery)

Sludge component	% by wt
Inorganic salts	8·3
Carbon	Trace
Acetone insoluble organics	5·4
Acetone soluble organics	6·2
Water and water solubles	0·1
Oil	80·0

A more detailed analysis is given in Table II, from which it appears that the carbon–hydrogen ratio of the acetone insoluble resins is appreciably higher than for the acetone soluble ones, but that the difference in oxygen contents is relatively small.

TABLE II

Typical Sludge Analysis

Component	Organic material, % wt		Inorganic deposits, % wt
	Acetone * soluble	Acetone † insoluble	
Carbon	70·5	83·6	—
Hydrogen	7·9	3·0	—
Oxygen	12·7	10·9	—
Nitrogen	1·7	1·0	—
Sulphur	2·4	1·5	—
Iron	0·6	—	4·7
Lead	1·4	—	—
Chlorine	0·8	—	—
Bromine	2·0	—	—
Lead halides	—	—	79·2
Lead sulphate	—	—	16·1

* Low molecular weight resins.
† High molecular weight resins.

It is abundantly clear from these results that sludge is not a simple dispersion of carbonaceous particles in oil, and that experimental work undertaken with the object of elucidating the effects of oil additives on it could be misleading in its practical significance if carbon black only were used as a model substance. Earlier work in this field,[2–5] culminating in that of Garner and co-workers,[6–11] although contributing greatly to the elucidation of the nature of sludge dispersions, lays itself open to this criticism. These workers have demonstrated the analogy between electrokinetic phenomena of carbon black suspensions in organic liquid media and of colloidal suspensions in aqueous systems. They have shown that these phenomena play an important role in the stability of carbon black suspensions and that they are more marked in liquids of the greatest detergent efficiency.[9]

In all the experiments which follow, Standardized Oil Filter Test Contaminant No. 1 has been used. This material is available from the Pontiac Testing Laboratory and consists of sludge filtered from used engine oil and re-dispersed in straight mineral oil. The particle size of the solids present is predominantly in the range 0 to 2 microns. An analysis of the material used is given in Table III. Before use the sludge was dried to less than 0·05 per cent water content by stirring at 135° C in an open beaker.

TABLE III

Composition of Pontiac Standardized Oil Filter Contaminant No. 1

Sludge component	% by weight
Inorganic salts (mainly lead)	4·9
Acetone insoluble organics	6·9
Acetone soluble organics	1·8
Water and water solubles	1·0 (max)
Oil	85·4
Particle size analysis	**% of total**
0–2 microns	94·5 ± 2
2–5 microns	5·0 ± 2
5–10 microns	0·4 ± 0·1
10 +	0·08 ± 0·02

The present work has been concerned with the measurement of the electrophoretic mobility of engine sludge in oil solutions of additives. The charges conferred by different dispersant additives on the sludge particles have been determined and the effects of viscosity and temperature on the electrophoretic mobilities for three types of additive investigated over a limited temperature range. These effects have been related to the ability of the additives considered to maintain engine sludge in suspension.

EXPERIMENTAL

A Tiselius type U-tube, which is illustrated in Fig 1, was used in the electrophoresis experiments. The tube had a third limb which joined the U-tube at the bottom of the bend and which assisted in the filling procedure. A clear solution of additive in oil was poured into the tube and then a suspension of the dried engine sludge in the additive oil solution was added through the third limb until the lower half of the U-tube contained the suspension. A potential of 80 volts/cm from a stabilized d.c. power supply was applied to the solution by means of platinum disk electrodes suspended in the clear supernatant additive oil layer. The tube was immersed in an oil bath which was controlled to ±0·1° C, and movement of the sludge layer was observed with a cathetometer,

the arrangement of the apparatus being shown in Fig 2. The boundaries move at a rate determined by the electrophoretic velocity and the settling velocity. The settling velocity was eliminated by taking the mean of the rates of boundary motion in both limbs of the U-tube, and hence the electrophoretic mobility

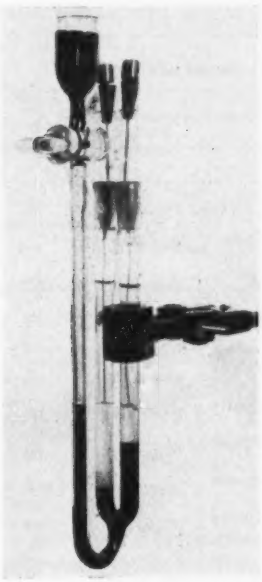

FIG 1

U-TUBE USED FOR ELECTROPHORETIC EXPERIMENTS

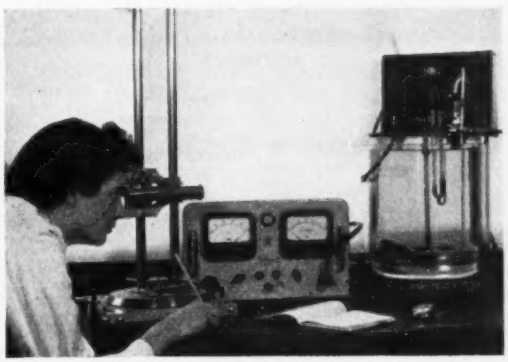

FIG 2

GENERAL ARRANGEMENT OF ELECTROPHORETIC APPARATUS

obtained from its definition as the electrophoretic velocity per unit potential gradient.

The settling experiments were carried out by thoroughly agitating, with a commercial rotary food mixer, 90 g of a sample of additive oil and 10 g of engine sludge in a beaker at 93·3° C. The mixture was allowed to settle for 24 hours in a vertical glass tube (3 × 38 cm) maintained in an oil bath at 93·3° C. At the end of this period, the upper 25 ml of the mixture were carefully pipetted off and analysed for the presence of sludge by diluting with 75 ml of *n*-heptane and centrifuging. The results were expressed as the percentage of sludge found to that which would have been present had no settling occurred. Thus a value of 100 per cent would indicate that no settling had taken place.

RESULTS

Preliminary Experiments

A few preliminary experiments were carried out at room temperature in a mixture of a solvent refined paraffinic distillate oil (kinematic viscosity : 5·1 cS at 98·9° C) and benzene mixed in the ratio 3 : 2 by weight. An additive concentration of 10 per cent wt was employed together with 3 per cent wt of sludge. The results confirmed that some dispersant additives confer positive charges on the sludge particles and some additives confer negative charges. The data obtained are given in Table IV.

TABLE IV

Polarity of Sludge Dispersions in the Presence of Additives

Additive	Polarity of sludge
Calcium sulphonate	−ve
Sulphurized hydrocarbon	−ve
Vinyl ester copolymer (Type I)	−ve
Sulphurized barium phenate	+ve
Phosphosulphurized hydrocarbon	+ve
Vinyl ester copolymer (Type II)	+ve

From this it can be seen that when a commercial calcium sulphonate additive was dissolved in the oil–benzene mixture the sludge suspension moved towards the anode. A sulphurized hydrocarbon also conferred a negative charge. On the other hand, when additives such as a sulphurized barium phenate or a phosphosulphurized hydrocarbon were added to the solvent the sludge suspension moved towards the cathode. It is interesting to note that these electrophoretic effects were observed not only with metal-containing additives but also with entirely organic ones. Other organic additives which were tested, besides the sulphurized and phosphosulphurized hydrocarbons, were certain vinyl copolymers, and with these very small boundary movements were observed. An experiment was also made with no additive present, but no satisfactory measurements of boundary movement could be made because the engine sludge fell out of suspension too rapidly.

All the dispersant additives mentioned above gave a sludge dispersancy value of at least 60 per cent when tested by the standardized procedure previously described using a solvent-extracted SAE 30 paraffinic

oil as the suspension medium. As has been shown previously in the case of carbon black dispersions by Garner, Nutt, and Mohtadi [10] and also van der Minne,[12] it was observed that mixtures of equal parts by weight of additives with opposing electrophoretic mobilities tended to coagulate rather than to peptize engine sludge. This is illustrated in Table V, where it may also be seen that this effect occurs irrespectively of whether or not the additive is entirely organic or is metal-containing in nature.

TABLE V

The Effect of Mixing Additives on Sludge Dispersancy

Component Additives *			Equal mixture of † additives
Type	Sludge polarity	Sludge dispersancy, %	Sludge dispersancy, %
Phosphosulphurized hydrocarbon	Positive	80	18
Sulphurized hydrocarbon	Negative	88	
Sulphurized barium phenate	Positive	60	20
Calcium sulphonate	Negative	90	
Sulphurized barium phenate	Positive	60	15
Sulphurized hydrocarbon	Negative	88	
Phosphosulphurized hydrocarbon	Positive	80	83
Sulphurized barium phenate	Positive	60	
Calcium sulphonate	Negative	90	70
Sulphurized hydrocarbon	Negative	88	
Nil	—	3	—

* 2·5% wt concentration in the additive oil.
† 5% wt concentration of the mixed additives in equal amounts in the additive oil.

It was observed, however, that there was a noteworthy exception to this general effect. This occurred when at least one of the components of the additive mixture was one of several types of vinyl ester copolymer. In these cases a high degree of sludge dispersancy was retained for the mixture of additives, no matter what type of additive amongst the ones tested formed the second component. Some typical results are given in Table VI.

It became likely therefore that the way in which the two classes of additives dispersed engine sludge were distinct in some respect, and a more detailed study of their electrophoretic behaviour was undertaken.

Electrophoretic Mobilities

Approximate preliminary determinations of the value of the electrophoretic mobilities were made at room temperature (16°–18° C). In these experiments the conditions previously described were used, except that a constant temperature bath was not employed. Even so, it was at once apparent that the mobilities of the vinyl ester copolymers were much lower than the other additives tested, and it was suspected that this might be related to the kinematic viscosity of the dispersions as shown in Table VII.

TABLE VI

The Effect of Mixing Additives on Sludge Dispersancy

Component additives *			Equal mixture of † additives
Type	Sludge polarity	Sludge dispersancy, %	Sludge dispersancy, %
Phosphosulphurized hydrocarbon	Positive	80	75
Vinyl ester copolymer (Type I)	Negative	63	
Sulphurized barium phenate	Positive	60	70
Vinyl ester copolymer (Type I)	Negative	63	
Calcium sulphonate	Negative	90	70
Vinyl ester copolymer (Type I)	Negative	63	
Vinyl ester copolymer (Type II)	Positive	85	55
Vinyl ester copolymer (Type I)	Negative	63	
Vinyl ester copolymer (Type III)	Negative	100	80
Vinyl ester copolymer (Type I)	Negative	63	
Nil	—	3	—

* 2·5% wt concentration in the additive oil.
† 5% wt concentration of the mixed additives in equal amounts in the additive oil.

TABLE VII

*The Electrophoretic Mobility * and Viscosity † of Sludge Dispersions*

Additive type	Electrophoretic mobility × 10^5, cm^2/sec/volt at 16° C to 18° C	Kinematic viscosity, cS at 25° C
Sulphurized barium phenate	0·030	2·9
Phosphosulphurized hydrocarbon	0·020	3·8
Sulphurized hydrocarbon	0·020	8·3
Vinyl ester copolymer (Type II)	0·002	22·6

* 10% wt additive in 60/40% wt solvent extracted paraffinic distillate mineral oil (kinematic viscosity 5·1 cS at 98·9° C) and benzene to which were added 3% wt sludge. Determinations carried out at room temperature in a field of 80 V/cm.
† IP 71/55.

Elimination of Viscosity and Temperature Effects

Further experiments were designed to eliminate this viscosity effect between additives. It was desired to determine whether, at the same viscosity, different additives gave the same order of mobility.

Two routes were taken to achieve this: (1) the ratio of paraffinic oil to benzene was varied, and (2) the temperature was varied.

A graph of electrophoretic mobility against viscosity is given in Fig 3 for a sulphurized barium phenate

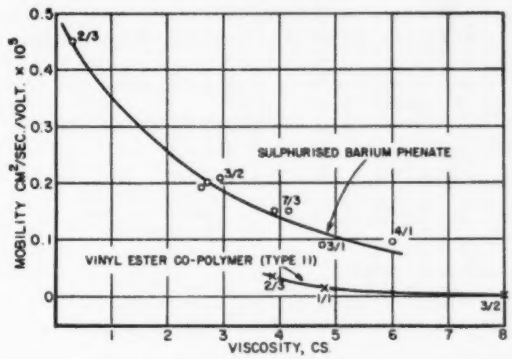

FIG 3

THE EFFECT OF VISCOSITY ON ELECTROPHORETIC MOBILITY USING DIFFERENT SOLVENT RATIOS AND CONSTANT TEMPERATURES

Temperature 50° C

Solvent ratio at each point: $\frac{\text{Parts by wt paraffinic oil}}{\text{Parts by wt benzene}}$

Dry Pontiac sludge 3% wt
Additive 10% wt

additive and a vinyl ester copolymer. The temperature was kept constant and the viscosity varied by varying the oil–benzene ratio. It can be seen from the graph that the mobility caused by the polymeric additive at any particular viscosity is lower than that caused by the sulphurized additive. It was thought, however, that this curve might not be a true mobility–viscosity relationship due to the increasing solvent polarity with increasing amounts of benzene in the solution. This might affect the conclusions drawn regarding the mobility of the sludge with the polymeric additive compared with the sulphurized one, because at the same viscosities the solutions containing the two additives had widely different compositions.

The relationship between sludge mobility and viscosity for sulphurized barium phenate at a constant oil–benzene ratio of 3 : 2 over a range of temperature is given in Fig 4. Two points are plotted for a polymeric additive solution, but at the highest temperature which could be used without trouble from evaporation losses (about 60° C), the viscosity of the polymeric additive solution did not come within the viscosity range of the sulphurized barium phenate solution.

From this graph no conclusions can be drawn regarding the mobility at the same viscosity of the two types of additive considered, but it is interesting to note that over the short viscosity range produced by changing the temperature, the mobility varied linearly with the viscosity for the sulphurized barium phenate, but was independent of viscosity for the polymeric additive.

To determine whether the change in mobility depended solely on the change in viscosity or whether there was also some temperature effect, it was desired to produce two solutions of a particular additive with the same viscosity at different temperatures. This was achieved by using cetane and heptane, both of which, being paraffins and varying only in chain lengths, were not expected to give different polarity effects.

Measurements were made of the electrophoretic mobility of sludge suspensions in oil containing sulphurized barium phenate at a constant temperature of 50·1° C, but with varying ratios of heptane to cetane. These results are shown by the circles in Fig 5. Similar measurements made at a lower temperature of 35·6° C gave results for the same additive (indicated by crosses) which fell on the same curve. This indicates that for this type of additive and over this temperature range there is no effect of temperature on the mobility. Further measurements using

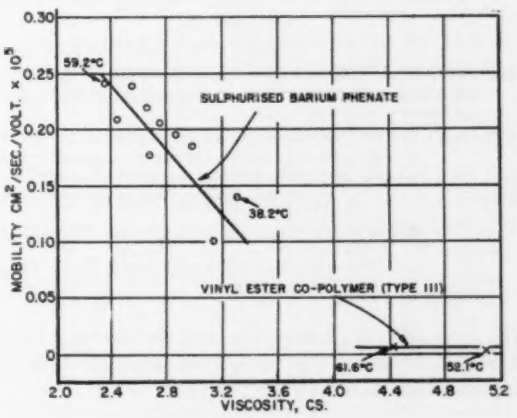

FIG 4

THE EFFECT OF VISCOSITY ON ELECTROPHORETIC MOBILITY USING DIFFERENT TEMPERATURES AND CONSTANT SOLVENT RATIOS

Solvent ratio: $\frac{\text{3 parts by wt paraffinic oil}}{\text{2 parts by wt benzene}}$

Dry Pontiac sludge 3% wt
Additive 10% wt

a phosphosulphurized hydrocarbon additive at 35·6° C (dotted circles) showed that results with this additive also fell on the same curve.

However, the sludge suspensions in the polymeric additive oil solutions gave lower mobility values than suspensions in the metal-containing sulphurized barium phenate and metal-free phosphosulphurized additive solutions and, moreover, they did appear to show a temperature effect. Thus at 35·6° C the mobilities were considerably lower than at 50·1° C.

In addition, the values obtained for the polymeric additives fell on a different curve from the non-polymeric ones. However, it must be mentioned that measurements on polymeric additives are more inaccurate than with the other types, not only because the movement is smaller, but because the boundaries are diffuse, since the sludge suspensions tend to separate into dark and faint layers.

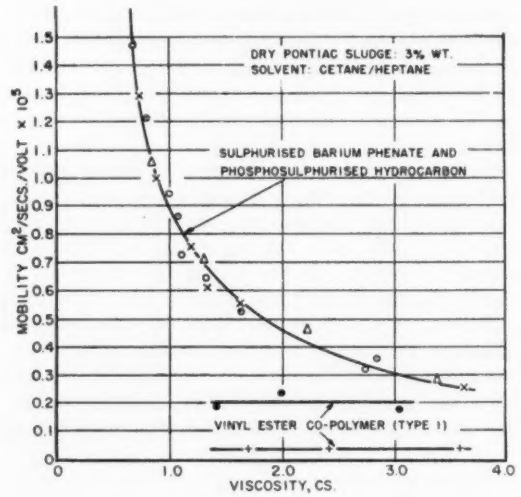

FIG 5

THE EFFECTS OF VISCOSITY AND TEMPERATURE ON ELECTROPHORETIC MOBILITY USING DIFFERENT ADDITIVES AND DIFFERENT SOLVENT RATIOS

Additives: O—10% wt sulphurized barium phenate at 50·1° C
×—10% wt sulphurized barium phenate at 35·6° C
△—5% wt sulphurized barium phenate at 35·6° C
○—10% wt phosphosulphurized hydrocarbon at 35·6° C
●—10% wt vinyl ester copolymer (Type I) at 50·1° C
+—10% wt vinyl ester copolymer (Type I) at 35·6° C

Additive Concentration Effect

Some measurements were made of the electrophoretic mobility of sludge suspensions in heptane–cetane of sulphurized barium phenate at three concentrations. The results obtained are tabulated in Table VIII. They show that decreasing the additive concentrations from 10 per cent wt to 5 per cent wt has no effect on the mobility, but that a decrease in mobility does occur on decreasing the concentrations a further tenfold to 0·5 per cent wt. It thus seems that a saturation limit of additive concentration is reached, above which no increase in mobility occurs.

Relation between Electrophoretic Mobility and Sludge Dispersancy

In the case of the non-polymeric additives tested, a fair correlation between the electrophoretic mobility of the sludge and the relative sludge hold-up in the dispersancy test has been obtained. This applies to both metal-free and metal-containing additives and to a variety of additive mixtures. The correlation is illustrated in Fig 6. The mobilities were determined

TABLE VIII

The Effect of Additive Concentration on Sludge Mobility

Solvent: 40/60% wt heptane–cetane
Dry Pontiac sludge: 3% wt
Additive: Sulphurized barium phenate
Temperature: 35·6° C

Additive concentration, % wt	Electrophoretic mobility × 10^5, $cm^2/sec/V$
10·0	0·54
5·0	0·54
0·5	0·43

at room temperature under a field of 80 V/cm using a 60/40 per cent wt mixture of a solvent extracted paraffinic distillate mineral oil of 5·1 cS kinematic viscosity at 98·9° C and benzene. To this were added 10 per cent wt of the respective additives and 3 per cent wt dry sludge. The sludge dispersancies were determined by the standard procedure using 5 per cent wt of additive in an SAE 30 grade solvent extracted paraffinic lubricating oil at 93·3° C.

The correlation between the mobility imparted by individual additives and their mixtures with the corresponding sludge dispersancy is illustrated by the results given in Fig 7. It will be seen that for non-polymeric additives, additives of opposing charge impart a reduced mobility to sludge, and this is reflected by a reduced sludge dispersancy. Again this applied to both metal-free and metal-containing additives. When at least one of the additive components is a vinyl ester copolymer, however, it can be seen that although the initial mobilities and also the residual mobilities after mixing are very low, the mixed additives have a high sludge dispersant ability.

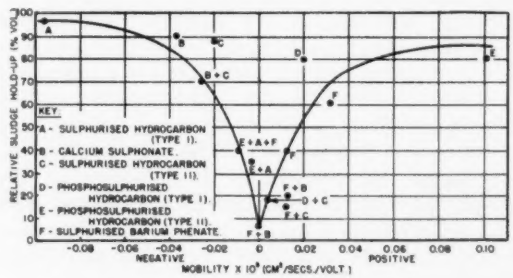
RELATIVE SLUDGE HOLD-UP (% VOL.)
KEY
A - SULPHURISED HYDROCARBON (TYPE I).
B - CALCIUM SULPHONATE.
C - SULPHURISED HYDROCARBON (TYPE II).
D - PHOSPHOSULPHURISED HYDROCARBON (TYPE I).
E - PHOSPHOSULPHURISED HYDROCARBON (TYPE II).
F - SULPHURISED BARIUM PHENATE.
NEGATIVE
POSITIVE
MOBILITY X 10⁵ (CM²/SECS./VOLT)

FIG 6

THE RELATIONSHIP BETWEEN THE ELECTROPHORETIC MOBILITY AND THE RELATIVE SLUDGE HOLD-UP OF ADDITIVE OIL SOLUTIONS

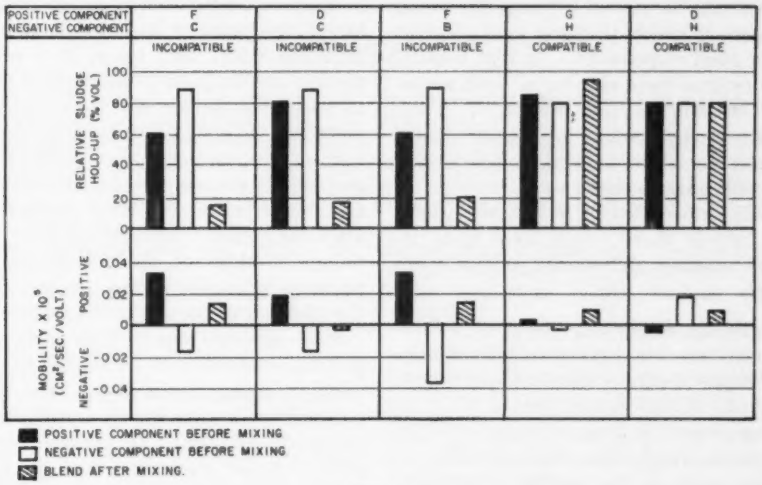

FIG 7

THE EFFECT OF ADDITIVE INTERACTIONS ON THE ELECTROPHORETIC MOBILITY AND SLUDGE DISPERSANCY

B—Calcium sulphonate
C—Sulphurized hydrocarbon
D—Phosphosulphurized hydrocarbon (Type I)
F—Sulphurized barium phenate
G—Vinyl ester copolymer (Type II)
H—Vinyl ester copolymer (Type III)

DISCUSSION

From this work emerges the fact that in many cases electrokinetic phenomena play a large part in the stability and sedimentation behaviour of dispersions of engine sludge in lubricating oil. This applies when both metal-containing and non-metal-containing additives are used as dispersing agents, and is irrespective of the polarity imparted to the sludge. Similar phenomena exhibited by carbon black when dispersed in a variety of liquid media have been fully discussed in a series of papers by Garner and co-workers [6–11] and theories put forward to account for the settling and electrokinetic behaviour of such dispersions. These authors conclude that dispersions of carbon black in organic liquids may be classed into three groups, namely:

(1) Dispersions which settle rapidly after a short induction period. These are also characterized by a sharp liquid-dispersion interface and a large final sediment volume.

(2) Dispersions which settle very slowly, have no interface, and have a small final sediment volume.

(3) Non-settling dispersions.

The settling characteristics of the dispersions in group (1) are explained by the prior formation of a chain and scaffolding network of carbon particles throughout the liquid. This then gradually collapses through the aggregation of further carbon particles under Brownian movement overloading it at its weak points. In order to form an aggregate, a particle has to overcome an energy barrier proportional to the work done in displacing a mass of liquid located between it and the scaffolding against surface tension. That is:

$$E \propto \rho\gamma$$

where E is the energy barrier, ρ is the density, and γ is the surface tension. Hence, as $\rho\gamma$ for different systems become larger, a greater energy barrier has to be overcome, and a slower rate of settling is produced. On this basis, therefore, dispersions in group (2) are of such a type that the energy barrier for aggregation can only be overcome with some difficulty by the particles under Brownian movement, whilst for those in group (3) the energy barrier is sufficiently high to make the rate of settling infinitely slow. When the sedimentation rate is sufficiently slow, only small concentrations of aggregated particles, which are just large enough not to be kept in suspension by Brownian movement, will settle. Under such conditions, the formation of scaffolding by the interaction of aggregates will not be favoured and the liquid dispersion boundary will be diffuse.

If a dispersion of sludge in oil containing an additive exhibits electrokinetic phenomena, this is evidence for the presence of an electrical double layer at the sludge–liquid interface, even though the origin of electrical double layers is uncertain in media which do not encourage ionization. It may, for instance, be due to the orientation of polar additive molecules adsorbed on the sludge. The energy associated with the electrical double layer will increase the surface tension and hence also the energy barrier for aggregation.

Since this will decrease the rate of settling, one would expect that materials which promote electrokinetic phenomena to be good dispersants. In Figs 6 and 7 this is shown to be true for a number of both metal-containing and entirely organic additives. These figures also illustrate the marked interactions which can occur on mixing additives which individually confer opposing polarities to sludge.

It has now been shown that in certain vinyl ester copolymers, of which three types have been investigated, some marked differences in behaviour exist. These are:

(*a*) High sludge dispersant power is accompanied by relatively low electrophoretic mobility.

(*b*) Only slight sludge sedimentation is produced in binary additive mixtures of which at least one component is from a group of vinyl ester copolymers, irrespective of the polarity imparted to the sludge by the individual additives when used alone.

(*c*) The electrophoretic mobility of the sludge is temperature dependent in the range studied.

(*d*) The electrophoretic mobility of the sludge is little, if at all, dependent on viscosity in the range studied.

These effects are directionally opposed to those obtained for non-polymeric additives used to disperse engine sludge, whose behaviour agrees essentially with that described by others for carbon black dispersions.

From the relation between the electrophoretic mobility and zeta potential (ζ) given by:

$$\text{Electrophoretic mobility} = \zeta \cdot \frac{\varepsilon}{4\pi\eta}$$

where ε is the dielectric constant of the medium and η its viscosity, it could be inferred that, for a given viscosity and zeta potential, a smaller electrophoretic mobility should be accompanied by a lower dielectric constant. That is, if two additives are highly effective in dispersing sludge in oil by endowing the sludge particles with high zeta potentials, but the two systems have widely different electrophoretic mobilities at the same viscosity, then it might follow that the system with the lower mobility would have a lower dielectric constant.

Although no measurements of dielectric constant were made, it is thought that this explanation of the low electrophoretic mobility and high dispersant power of the vinyl ester copolymers is unlikely in view of the results of previous workers,[9] who have shown that liquids of high dielectric constant are in general good dispersants.

Because of this, as well as the fact that in binary additive mixtures, of which at least one component is from the group of vinyl ester copolymers in question, no marked coagulation of sludge takes place irrespective of the polarity imparted to it by the individual additives when used alone, it is probable that the electric double layer present plays only a subsidiary or minor role in the stabilization of the sludge suspension. Although the implications of the dependence of the electrophoretic mobility on temperature and not on viscosity, as found for the group of vinyl ester copolymers, is uncertain, these effects, which are directionally opposed to those found for non-polymeric additives, also indicate the likelihood of the presence of an alternative mechanism to account for the stability of the sludge dispersions.

It is suggested that in these cases adsorption of the polymeric additive on the sludge occurs, and that the additive–sludge particles are then stabilized by solvation due to the highly lipophillic nature of the polymeric additive. In general, the polymeric additives under discussion are of higher molecular weight and of greater chain length than the non-polymeric ones. This fact would tend to favour their solvation by the hydrocarbon medium. Under these conditions the presence of an electrical double layer is of secondary importance, and the effect of added materials on the polarity and magnitude of the associated zeta potential would not be expected to have a pronounced effect on sludge sedimentation.

ACKNOWLEDGMENTS

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DISCUSSION

Dr J. B. Matthews: As pointed out by the authors, previous investigators, notably Professor Garner and his school at Birmingham, and Dr van der Minne in Holland, have studied electrokinetic phenomena in hydrocarbon systems, and this paper confirms the general conclusions reached by them. These are, of course, that hydrocarbon colloidal dispersions are analogous to aqueous colloidal systems in possessing zeta potentials and obeying the same laws of flocculation.

The justification for the present authors' contribution is that they have carried out their measurements on colloidal systems which are claimed to be more representative of real engine lubrication systems than those previously investigated.

I hope I will be forgiven, however, if I express a doubt on this claim, because I think it is a matter which could be usefully discussed.

The authors give analytical data on a typical sludge, which is 80 per cent oil and contains very little water. Low temperature sludge, as obtained in the Chevrolet FL-2 test referred to by the authors, however, usually contains an appreciable amount of water emulsified with the oil.

I do not want to press this point, but the nature of a typical sludge is probably worthy of further discussion. Whatever the real nature of the sludge (and this will vary according to operating conditions), the authors do not produce any data to show that there is any difference between results obtained with their sludge and those obtained by previous workers using carbon dispersions.

In view of the known experimental difficulties of measuring electrophoretic mobilities, the authors are to be congratulated on their results, which agree fairly well with those of van der Minne,* who used a more accurate apparatus in which the movement of a single particle is measured instead of a phase boundary.

Nevertheless, there are some features of the results which call for explanation.

For example, in Fig 3 the relationship between mobility and viscosity is not linear, as it should be theoretically. This may be due to a variation in the dielectric constant as the concentration of benzene in the system is varied. This is supported by the linearity of the curve obtained when the benzene concentration is kept constant, and the viscosity changed by altering the temperature. However, when the authors used mixtures of cetane and heptane as their dispersion medium, they again obtained a non-linear relationship between mobility and viscosity (Fig 5). In this case there can be little variation, if any, in the dielectric constant as the proportions of cetane and heptane are varied.

The temperature dependence of the mobility in the systems containing the vinyl ester copolymers is perhaps not surprising when one considers the nature of such polymer solutions. In hydrocarbon solution these polymer molecules, which contain polar groups all along their length, will be in a coiled state at low temperatures, and will uncoil themselves gradually as the temperature is raised, thus exposing more polar groups as the temperature rises. The authors' observations on the change of mobility with temperature can possibly be explained on this basis.

In the dispersancy test the sludge is dispersed in the SAE 30 oil by mechanical agitation in the presence of the additive. This test may therefore measure the ability of the additive to assist the dispersion of a coagulated sludge, rather than of the ability of the additive in preventing coagulation. The two types of behaviour are not necessarily equivalent—good dispersing agents in the true sense of the word are not always good stabilizers.

It would only be possible to use the test results as a measure of suspension stabilizing power if we were certain that all the dispersions in the freshly mixed state had the same particle size distribution. Some information on particle size in the actual dispersions would be useful and would perhaps give a truer picture of the flocculation taking place than the arbitrary criterion chosen by the authors.

It is not quite clear why the authors chose to measure their sludge stability in an SAE 30 oil when their mobility data were obtained in a much less viscous mixture of oil and benzene. Would it not have been more satisfactory to correlate stability and mobility data obtained with the same dispersion medium? Can the authors tell us if they made any observations on the stability in the benzene mixtures?

On the subject of stability the assumption is made, of course, that sludge separates out in the engine because the insoluble particles flocculate, and that unless flocculation takes place no sludge will separate. During engine operation the oil is undergoing continuous agitation, probably as violent as that produced by the food mixer used by the authors to disperse their sludge. Flocculation is therefore unlikely to occur, even in the absence of additives, except during long static periods. The flocs formed then are likely to be re-dispersed on starting up the engine again, and therefore there is good reason to believe that some factor other than flocculation is involved in the deposition of sludge. Some recently published work† shows that the relative adhesion energy of the particle and the oil medium for the metal surface is perhaps a more important factor than the flocculation of the particles themselves. To demonstrate that the zeta potential is important in sludge deposition, I think it would be necessary to produce correlations between zeta potential in the actual used oils and the cleanliness of the engines from which the used oils were taken. Transferring the sludge particles to different liquid media can alter their colloidal behaviour.

In spite of these criticisms, I think the authors have made a useful contribution to our knowledge of the possible ways in which suspensoids in hydrocarbon media can be stabilized. Their results raise the old question of the source of the zeta potential in colloidal systems of low dielectric constant. Obviously, we cannot rule out the presence of water in the present case because, although fairly dry sludge was used, the benzene was not dried and may have contained appreciable amounts of water.

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* van der Minne, J. L., and Hermanie, P. H. J. *J. Colloid Sci.*, 1952, **7**, 600; *ibid.*, 1953, **8**, 38.

† Clayfield, E. J., Matthews, J. B., and Whittam, T. V. Paper 1 in Boundary Lubrication Group 3, Institution of Mechanical Engineers Conference on "Lubrication and Wear," London, 1–3 October 1957.

The observed electrokinetic phenomena cannot be due to an oriented adsorbed layer of polar additive molecules, as the authors suggest. Such a model would give a fixed Helmholz double layer, but for the production of electrokinetic phenomena it is necessary to have a Gouy–Stern diffuse layer, which means that there must be some unbound ions present in the solution.

It is also unsafe to attribute colloidal stability to a high surface tension, as the authors do, because the surface tension of hydrocarbon oils is hardly affected at all by additives, even when they exhibit very large differences in stabilizing power. In any case, the flocculation of two particles in an oil cannot be affected by the surface tension of the oil unless the particles happen to be floating in the oil surface. What is important is the interfacial energy between the oil and the particle and the cohesive energies of the particles and the oil, which together define the works of adhesion between oil and particle and between one particle and another. It is probably the relative values of these two works of adhesion which determines the stability of the suspension.

Dr P. J. Agius: Dr Matthews asked whether there was any correlation between sludge sedimentation as measured by laboratory tests and that measured by engine tests. Without wishing to go into a lot of detail, and also simplifying the matter considerably, we have convinced ourselves that some additives which disperse sludge well as measured by laboratory tests also give clean engines under low temperature sludging conditions, whereas others that do not disperse sludge well, judged by laboratory tests, do not lead to clean engines. Although it is pleasant to think that the engine is agitating the sludge the whole time, in the same way as the food mixer used in the laboratory test, in fact some sludge sedimentation does occur under these conditions. Removing suitable parts, such as a crankcase or a cover plate, will soon convince anybody of that.

Now to consider the actual sludge used. This is a difficult thing to discuss, because sludge is far from being a chemical entity. Whenever one starts doing work on a particular type of sludge, someone else is almost certain to have used or be using another kind, and will claim that his kind is much more realistic. Whatever views one has on the constitution of sludge, it is certain that the sludge that we used did not consist of carbon particles. We moved right away from carbon and extended previous work into the field of engine sludge. The fact that some of the results which originally had been obtained for carbon by other workers were reproduced for sludge is very significant, as it means that some of those original theories can be put to practical use.

A word about the water content of sludge. Low temperature sludge can contain water, but it is not necessary. One can obtain quite a lot of sludge in the field, and on engine tests, in engines which have not been run at such a low temperature that it promoted the formation or the collection of water in the sludge. This is particularly so under cyclic test conditions, as distinct from the FL-2 conditions mentioned by Dr Matthews. The Pontiac sludge contains about one per cent of water. We dried it down further to a very low value, of about 0·05 per cent, to obtain constant experimental results. If dispersancy tests are carried out on sludge containing about one per cent of water, the dispersancy values are reduced to some extent and a certain lack of reproducibility is introduced. However, the trend of the results still holds, and the sludge was dried in the interests of reproducibility.

Pontiac sludge, as it used to be sold up to about 1951, was fairly consistent material. Here are some additional characteristic data to that given in the paper:

Chemical Analysis by Weight:	
Water	Max 1%
Petroleum ether insolubles	25 ± 1%
Petroleum ether solubles	75 ± 1%
Analysis of Petroleum Ether Insolubles	25 ± 1%
Chloroform solubles	3·5 ± 1%
Chloroform insolubles	22·5 ± 2%
Analysis of Chloroform Insolubles	22·5 ± 2%
Carbonaceous matter	16 ± 4%
Ash	8 ± 3%

The metallic constituents of the ash are mainly iron and lead, with trace amounts of a large number of other metals. The virtual absence of calcium and barium is noteworthy. Apart from this, an appreciable proportion of silicon, presumably from road dust, is also present.

Subsequent to that date, around 1954 and 1955, samples of Pontiac sludge started to contain an appreciable amount of calcium and barium. In other words, it is fairly obvious that the Pontiac laboratories were using detergent oils, and consequently there was a danger that the sludge had a "built-in" dispersant. Therefore, for this particular work, the later sludge was not much use, and we took care to use the original sludge free from calcium or barium. As mentioned before, we think this represents a good step forward from using straight carbon black.

Turning now to the origin of the zeta potential: this is certainly a very difficult question, as Dr Matthews has pointed out. It is obvious that in the case of what we call conventional additives there is certainly an electric charge, because of the associated electrokinetic behaviour. There must be a charge to account for this, but how it gets there is far from certain. Oriented adsorption has been suggested, which, as Dr Matthews points out, is not a very happy explanation. However, to account for a moving charge in the oil without recourse to ionization, it is possible to postulate the presence of free electrons, rather than ions. From the point of view of this work, although we would like to know the answer, it is not of crucial importance; our main point is that one can divide the additives into two groups according to their electrophoretic behaviour, and I think we have shown that fairly clearly.

SAE 30 oil was used for the dispersion tests to link up with engine tests that were being carried out at the same time. We did carry out some dispersion tests with oils diluted with benzene, and also with oils of lower viscosity. In the cases where sedimentation of the sludge occurred, the effect was more marked with the diluted oil, but in the case where slight or no sedimentation took place, no increase in sedimentation was observed with the diluted oils, in spite of their lower viscosity.

To determine the effects of degree of dispersion on sedimentation behaviour different degrees of stirring with the food mixer were used. This was done by stirring for various times from a few seconds up to half an hour. There was a period up to a few minutes for which the sedimentation behaviour did depend on the degree of dispersion, but after that time the results were substantially independent of the amount of stirring which had taken place. It seems that the degree of dispersion was constant after these few minutes, irrespective of the amount of further stirring. That is the amount we settled on; the actual value used was 15 minutes at about 1500 rev/min.

Dr C. W. Nutt (part written, and in collaboration with Prof. F. H. Garner and Dr M. F. Mohtadi): First, the authors should be congratulated on a very clear and critical account of a project which provides a valuable contribution to our knowledge of the subject. Further, we agree with the authors that some danger exists in extrapolating our conclusions on the behaviour of "synthetic" carbon dispersions to sump oil sludges. However, for reasons which will be discussed later, we agree with Dr Matthews that this danger also exists with the work here reported, since it remains to be proved that sludge can be concentrated, dried, and re-dispersed to give a dispersion identical with the original. Nevertheless, the authors' findings are in good agreement with the results of some investigations we made on the electrophoretic separation of sludge from used oils. The oils examined were a representative range of commercial oils taken from various engines in all sorts of conditions. The experiments demonstrated pronounced electrophoresis of the suspended sludge (both positive and negative) in many detergent oils. However, in at least one detergent oil the suspended sludge showed negligible mobility, as was also found for non-detergent oils. Some photographs of these engine sludges were shown in the discussion of the paper of F. T. Barwell, L. Grunberg, and D. Scott, *Instn Mech. Engrs* (*Proc. Auto. Div.*), 1954–5, 53–7.

It was also found that at least one of the samples showed a pronounced aging effect when standing in bottles in the laboratory; the electrophoretic mobility decreased considerably during a few days and could not be restored by shaking or stirring by hand. It was therefore essential to carry out the measurements on samples which had been freshly obtained from a recently used engine. These observations are very pertinent to quantitative conclusions which may be drawn from the behaviour of dispersions which have been prepared by the technique of separating, drying, and re-dispersing the sludge.

It is of interest to consider the cause of this aging effect. It seems reasonable to suppose that it is a consequence of aggregation of the particles. The effect of engine operation is apparently such as to prevent the aging, and probably, in the case of oil already partly aged by standing in the sump, to reverse the aging, Is the effect of engine operating a consequence of the shear to which the oil is subjected during use, thus producing a re-dispersion of aggregates, or is it due to the higher temperature in the engine, to the continuous production and adsorption of some stabilizing compound which undergoes decomposition on standing, or is the aging due to oxidation and polymerization products formed on standing? No such effect is reported by the authors, but it would be interesting to know whether their systems correspond to the fresh oil or to the aged oil. It may be of interest to test the effect of a more vigorous dispersing technique, such as the use of ultrasonics, on the properties of the dispersions used by the authors.

Most of the experimental results for the "ionic" detergent systems seem to be in excellent agreement with theory. The data of Fig 5 show that the product, mobility × viscosity, is constant and independent of cetane–heptane ratio and of temperature, as is required by theory when ζ is independent of temperature. In Fig 3 the product is not independent of oil composition, but increases slightly with viscosity. The discrepancy cannot be due to the change in dielectric constant as it is in the wrong direction, but it may be due to a decrease in ζ caused by decrease of the degree of adsorption of sulphurized barium phenate as the proportion of benzene in the solvent is increased.

However, the data of Fig 4, which give the relation between mobility and viscosity at various temperatures for a mixture of paraffinic oil and benzene containing sulphurized barium phenate, shows a discrepancy with other results and theory. The product, mobility × viscosity, increases with increase of temperature. The variation seems to be larger than the experimental error and implies an increase of ζ, *i.e.* an increase of degree of adsorption, with increase of temperature. This seems rather unlikely and is at variance with the other data discussed above. Further study of the influence of temperature on the two variables, *e.g.* consideration of the activation energies of the processes, may elucidate this.

It is worth considering in more detail the mode of operation of the polymer additives. It is reasonable to assume that these polymers are absorbed, by an active end group, to the carbon particles, leaving a long oleophillic "tail" waving in the oil phase.

In concentrated dispersions the tails of the adsorbed molecules could prevent contact and aggregation of particles by purely mechanical means. For this the chain length must be of the same order of magnitude as the distance between particles, and may thus be estimated. Taking the average particle diameter as 30 mμ, there are $5{\cdot}5 \times 10^{14}$ particles per cc in a dispersion containing 3 per cent by weight of sludge. The average distance between adjacent particles is thus $1{\cdot}2 \times 10^{-5}$ cm. For mechanical contact between the adsorbed molecules, assuming them to be straight and not coiled randomly, each polymer molecule should contain 400 carbon atoms and have a molecular weight of the order of 5000–6000. It would be interesting to compare this estimate with the experimental data on the additive. The approximations and assumptions made in the above estimation are not likely to affect the final estimate by more than a factor of two or three. Thus, with additives having molecular weights less than this value, in systems with the concentration specified, we would expect sedimentation to take place slowly and to yield finally a sediment having a volume controlled by the chain length. With additives of higher molecular weight no sedimentation would be possible, except in so far as packing of the "tails" of adjacent particles permits consolidation of the sediment.

If now the particle is in a dilute dispersion, when it moves it must drag its numerous tails with it through the liquid, and this may contribute a very large term to the total resistance experienced by the particle. Thus, settling under gravity and motion in an electric field will be hindered. It does not seem necessary to postulate a solvation effect in the sense that oil molecules are firmly attached to the particle, although no doubt some oil molecules are mechanically entrained. Increase of temperature will have a two-fold effect. First, it will permit easier motion of the "tails" through the oil. This process will be similar to the process of diffusion of a long chain molecule through the oil, or to the transport of momentum through the oil. A second effect of increase of temperature is to decrease the degree of adsorption of the additive on the particles. If we assume that the viscous drag of the particle itself is small compared to that of the tails, the net effect of temperature on the drag, *i.e.* on the electrophoretic mobility, M, is given by an expression of the form:

$$M = Ae^{-E_A/RT} \cdot e^{-E_V/RT} = Ae^{-(E_A + E_V)/RT}$$

where A is a constant, E_A the heat of adsorption of the additive, and E_V the activation energy for viscous flow

of the tails through the oil. In this expression the first exponential term allows for change of degree of adsorption with temperature, and the second exponential term allows for the effect of temperature on the viscous drag experienced by the tails. The ζ potential is assumed to be temperature independent, since it probably arises from some mechanism other than the adsorption of the polymer additive. The data of Fig 5 permit a quantitative test of this for the vinyl ester copolymer system. Taking the mobility at 50·1° C to be 0·2 and that at 35·6° C to be 0·04, $(E_A + E_V)$ may be estimated from the slope of the plot of log M *v.* $1/T$. The value found is 22 Kcal/g mol. Now for long chain hydrocarbons and for polymers, $E_V = 9$ Kcal/g mol. A value of 13 Kcal/g mol is not unreasonable for the heat of adsorption. Thus the experimental data is in reasonable agreement with the hypothesis. The concept would be tested more critically by an independent determination of E_A from measurements of the variation of the degree of adsorption with temperature.

It may be concluded therefore from this work that temperature is an important variable whose role is dependent on the type of additive employed and the mechanism involved. Its influence on the mode of operation of detergent additives should be the subject of further study, since no experimental results have so far been reported at temperatures comparable to those found under engine operating conditions.

Dr P. J. Agius: It is quite true in our experience that engine sludge does change its properties on aging. This again is one of the difficulties encountered in working with sludge and one way of overcoming it is to use some fairly old sludge and keep to the same batch. It is not only sludge that ages; in fact, if one filters off sludge from a used engine oil, and just lets the oil stand, it quite often throws down some more sludge. It seems that the polymeric processes which presumably produce the sludge can be quite slow, and can go on for a long time. Thus, used engine oil is not a static material, but something which is continually changing.

Professor Garner in his original work used ultrasonics for preparing his sludge dispersions. We thought at the time it was rather gilding the lily, and we did not use the method, as we had found that prolonged agitation with a food mixer over 15 minutes did not alter the results. Another reason was that we did not have suitable apparatus readily available, but I think it would be a very good idea to try ultrasonics and see whether the results are markedly affected by this extremely efficient method of dispersion.

Dr Nutt's calculations of the molecular weight of the polymers used are of interest. Their molecular weights determined by viscometric methods are in the range 15,000 to 25,000, which is on the upper limit of the value calculated from Dr Nutt's postulates.

The deduction of the heat of adsorption from the data of Fig 5 certainly gives a very reasonable value. It emphasizes the need for further results at a series of temperatures, particularly engine operating temperatures, and we are pleased to have been able to stimulate an interest in this aspect of the subject.

R. Courtel: Was any observation made concerning the electro-osmetic effect, *i.e.* a modification of the velocity of the liquid near the walls of the tube?

Is the concentration of the additive at the place where the mobility is observed, *i.e.* at the separation surface, the same as in the bulk of the sludge suspension?

Was the effect of the concentration of additive studied in more detail, *i.e.* for many more values?

This question is of great interest to us at the Institut Français du Pétrole, because last year we developed an apparatus to study electrophoretic mobility of particles in used oil, at any concentration of additive and any

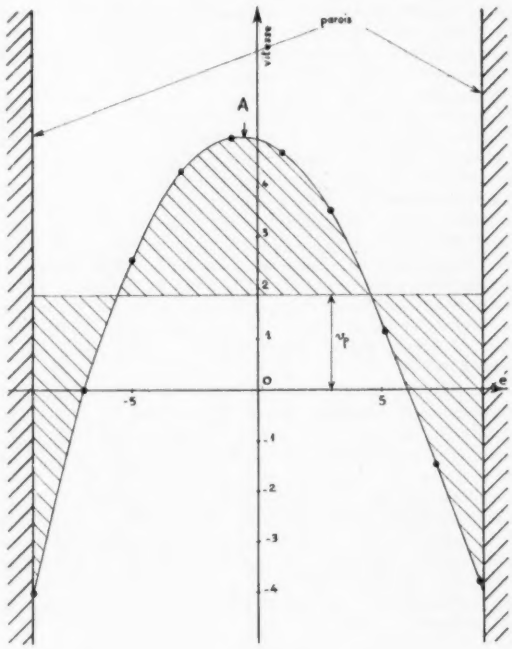

FIG A

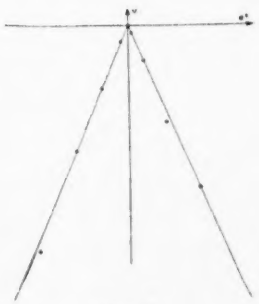

FIG B

temperature between room temperature and 200° C. This apparatus is quite different from that of Dr Agius,* and the results are not yet published. The accuracy of the measurements made by M. Briant, who is engaged on that work in our laboratory, appears to be very good. There is accuracy and correlation between the measured values and the calculated values that were made from electrophoresis and electro-osmotic effect and the

* The apparatus is adapted from that of Cotton and Mouton (1906). *C.R.Ac.Sc.*, 1904, **138**, 1584–6; *J. Chim. Phys.*, 1906, **4**, 363; "Les Ultramicroscopes et les Objets Microscopiques," Paris: Masson Editeur, 1906.

agreement is fairly good. We are now performing these measurements in connexion with results we gained from the C.B.L. method of aggregation of particles with temperature * and also with data obtained from some diesel and gasoline engines.

The two illustrations will give an idea of the accuracy of the measurement.

On the left and right of Fig A are the walls of the tube. The velocity zero is along the horizontal line, *i.e.* in the plan, which is traversed by the same number of carbon particles on one side and the other.

Fig B is the same graph with change of variables, *i.e.* velocity as ordinate and the square of space as abscissa. As can be seen the points are in a straight line, which means that the measurement is fairly accurate.

Dr P. J. Agius: Here are a few results which show the effect of additive concentration on electrophoretic mobility. They are taken from Table VIII of the paper. It can be seen, taking the case of the sulphurized barium phenate which I suppose can be called an ionic additive, that the concentration can be reduced by half and have no measurable effect on electrophoretic mobility; yet if it is reduced by tenfold again, the mobility drops from 0·54 to 0·43. These values are significantly different. From then on there is presumably an effect of additive concentration on mobility, but it can be swamped by using a sufficient additive concentration relative to the amount of sludge. In this work we used additive concentrations of around 3 and 5 per cent, so that the effects of changes of concentration would be very small.

R. Courtel: The reason for my question is that we have much more difference when we had a different concentration.

Dr P. J. Agius: That may be because you were using a different sludge concentration in relation to the range of additive concentrations. I think that not only the additive concentration, but also the ratio of this concentration to that of the sludge may be of importance.

R. Courtel: In any case, we have curves in which the general line is like a Gauss curve with a maximum, two lines increasing and decreasing. The maximum generally takes place not after 5 and 10 per cent but for lower concentrations. That is the reason why I asked if you had measurements in more detail.

Dr P. J. Agius: We have no measurements available in greater detail.

M. Courtel brought up the part of additive depletion. One would expect to find some depletion at the sludge additive boundary, on the assumption that the additive gets adsorbed on the sludge, but this does not seem to be an effect which one can measure very easily. However, with the more accurate work that M. Courtel is going to produce with his excellent apparatus, we can look forward to some published information on that aspect. As far as I know, no one has approached that side of it at all.

R. Courtel: We hope to publish the information in the *Compte Rendus de l'Académie des Sciences*. The apparatus is not a very new one, but it is quite different from yours.

Dr M. F. Mohtadi: I am surprised at the high concentration of additive that has been used in this work. In his work with Professor Garner, in 1948, Baddeley showed that a saturation level of additive was reached round about 1 or 2 per cent using the same range of concentration of suspended matter. This was later confirmed by further work on carbon black dispersions, using a number of commercial additives. A definite saturation value was reached in most cases around 1–2 per cent additive concentration. I wonder why the present authors used concentrations as high as 5 and 10 per cent for this work.

The second point is with regard to the effect of the stirrer used. Here again in the work on Micronex (carbon black) it was clearly shown that different types of stirrers gave different efficiencies of dispersion, as shown by examination of the samples under a microscope or an electron-microscope. For instance, using Micronex with average particle diameter of 28 mμ, when an ordinary mechanical agitator was employed, the smallest carbon aggregates in dispersion were round about 300 mμ, but when ultrasonic agitation was used for the preparation of the dispersion the average size of the carbon aggregates was reduced to approximately 50 mμ. I can remember the occasion of an IP meeting many years ago during which it was mentioned that we had used a supersonic agitator for preparing carbon dispersions at Birmingham University. Someone suggested that the academic mind had over-reached itself. But it was not really too academic to use a supersonic agitator for work of this kind, because it certainly showed very high dispersing power and efficiency.

In regard to the work done in Birmingham on carbon dispersions, one of the reasons why carbon black was chosen was that quite numerous references on studies of used lubricating oils had shown that most of the suspended solids were "carbonaceous," and that at least some carbon was present in the used lubricating oil. I am surprised to learn that only traces of carbon are found in Pontiac sludge and that most of the suspended matter is inorganic in nature.

Finally, may I suggest that it would have been extremely useful if the dispersancy tests in the present paper could have been confirmed or complemented by micrographs showing the actual state of aggregation of the particles in the dispersions? This would have been particularly important from the point of view of comparing the two systems, *i.e.* vinyl ester copolymers and the ionic additives.

Dr P. J. Agius: Answering the last question first, we have not as yet any photomicrographs, but following the excellent lead given by Professor Garner and his team when they did their earlier work, we intend trying to get some to see if there are any differences.

With respect to the concentration of additives used for the work, I think there is a slight misconception. Most of the electrophoretic work was done with a 3 per cent additive concentration. If one compares the results of Garner with ours for similar additives, he obtained less sedimentation with carbon black than we did with sludge. For example, when we used a well-known additive such as sulphurized barium phenate, and carried out sedimentation experiments over a series of concentrations from, say, a half per cent up to 10 per cent, we obtained a rising dispersancy curve to about 3 or 4 per cent, which then remained sensibly constant. So that from 3 per cent onwards the dispersancy curve is more or less flat and a saturation value is reached. Hence, by using additive concentrations of 3 per cent and above, we avoided the effects of concentration on dispersancy.

* Courtel, R., Bernelin, B., and Larbre, J. *Rev. Inst. franç. Pétrole*, 1955, **10**, 477–86.

In regard to the use of ultrasonics for dispersing sludge, I think it would be a good idea to see what effect this would have. However, it is rather hard to see the application of ultrasonic dispersing on sludge in an engine. After all, an engine is a mechanical system, and any dispersion caused by its rotating parts is probably far removed from ultrasonic effects. So although it would be extremely interesting, it is difficult to see any bearing on practical results.

Dr L. Grunberg: The normal way of assessing additives is engine cleanliness. I think one ought to try to speculate whether or not electrophoretic effects could occur in an engine and what influence these may have on cleanliness. The authors have shown that the electrophoresis of additive–sludge complexes was observable with electric fields of the order of 100 V/cm. It does not seem unlikely that in small clearances, say of the order of 0·1 mm, and with a contact potential between metal surfaces of about 1 V, fields of such strength would exist. In the case of ionic additives the particles would be driven from one surface to the other, according to the direction of the electric field. If this mechanism affected engine cleanliness one would expect a difference between ionic additives, which show high electrophoretic mobility, and polymeric additives, which have a rather low electrophoretic mobility. The two types of additive should show different degrees of engine cleanliness. Is there anything in the authors' data which would bear that out?

Dr P. J. Agius: Dr Grunberg has raised a very intriguing point; perhaps one ought to incorporate electrophoretic cells in the engine to increase the effect. It would be expected that additive–sludge complexes of low electrophoretic mobility would deposit less sludge in an electric field. We have found in practice that in many cases engine cleanliness is very good in these conditions, which are promoted by the use of polymeric additives. That is not to say, however, that the ionic additives do not also give clean engines, and it seems fair to mention that the evidence is not clear-cut either way.

It used to be reported in the early days of detergent additives that there was a danger that, after driving a certain mileage, detergent action collapsed and the engine became choked with sludge. I do not think that these reports were very well substantiated, but it is just possible that, with an ionic type of additive charge, neutralization might suddenly occur for some reason and the sludge would then be rapidly precipitated. It would be of interest to hear if anyone has any direct experience of this type of phenomenon.

A. G. Bell: Much criticism of the authors' work has arisen from the way in which they have prepared an artificial oil by taking a sludge or filter solid, drying it, and then trying to re-disperse it in new oil. Surely it would be possible to employ the original used oil for the experiments, and thereby obtain the solids of the correct chemical structure and the correct size distribution. I can see that the aging of a used oil could prevent this being done, but as they already employ aged sludged solid they could possibly use an aged oil.

If I use one type of oil in my engine and then add one of a different type, will the oil insolubles already in suspension be precipitated? In other words, are there any details of engine tests which show that this interaction does in fact play a part in the suspension of sludges in a gasoline engine?

Dr P. J. Agius: The first point is a very good one and, except for aging effects, is quite practical. In fact, although we have not given the data, we did carry out a few experiments on engine sludge taken straight from used crankcase oil. This was done by removing sludge from a crankcase, dispersing it in oil in the usual way, and carrying out dispersion tests or electrophoretic measurements. By and large, we got the same qualitative results but the reproducibility was rather poor. By keeping to the one batch of Pontiac sludge we obtained a consistent series of values, and this was our main justification for doing it. But one can get the same qualitative effects by using engine sludge straight from engines.

With regard to mixing different proprietary oils, one never knows what different formulations are involved, and the safest course is presumably to keep to one brand of lubricant.

J. B. Matthews: Does aging really alter the results? In practice, of course, one has fresh oil in the engine and the sludge is fresh, whereas all the authors' measurements have been made on aged sludge in order to get constant values. Does Dr Agius, therefore, think that his results will represent those to be expected in the engine?

Dr P. J. Agius: To answer this question fully, it would be necessary to carry out a series of measurements on sludge as it gradually ages and critically compare the results. This has not been done. However, from the qualitative agreement between results on fresh sludge and the more accurate data obtained on a single batch of aged sludge, it is not thought that the results are unrealistic in terms of what is to be expected in an engine. That is not to say that some differences in degree might not be found, and it would be desirable to obtain more data on this point.

Dr A. S. Freeborn: I would like to ask whether anything is known about sludge formation with ester lubricants, referring to the use of esters in a crankcase?

Dr P. J. Agius: It has been found that engines run on esters keep rather free from gum and varnish due to their solvent action. However, sludge is still formed by the polymerization of fuel-derived unsaturates, but I think it has been reported that it tends to be peptized and does not deposit as readily as with hydrocarbon oils. This is presumably due to the polar nature of the ester molecules and the possible presence of high molecular weight components.

A vote of thanks to the authors was accorded with acclamation.

THE FISCHER–TROPSCH SYNTHESIS WITH IRON CATALYSTS: THE EFFECT OF REACTION TEMPERATURE ON PRODUCT COMPOSITION*

By D. GALL† and P. J. KIPPING†

SUMMARY

Chromatographic methods of analysis have been used to investigate the effect of reaction temperature on the composition of the products of the Fischer–Tropsch synthesis. With increase in temperature over the range 200° to 300° C the mean molecular weight of the product falls and the proportion of oxygen compounds decreases in favour of olefinic and aromatic hydrocarbons. Analysis of the C_5 to C_8 paraffin and olefin fractions and the C_4 to C_5 alcohols by gas–liquid partition chromatography has shown that the proportion of branched-chain isomers increases regularly with synthesis temperature. The magnitude of the variation is of the same order as that brought about by a major change in the nature of the catalyst employed.

INTRODUCTION

THE products of the Fischer–Tropsch process for the synthesis of liquid fuels and chemicals from carbon monoxide and hydrogen consist in the main of olefinic and paraffinic hydrocarbons of a wide range of molecular weight, together with aliphatic oxygen compounds such as alcohols, acids, esters, etc. The effect of the process variables, *e.g.* nature of catalyst, reaction temperature, and pressure, on the characteristics of the products has received extensive investigation,[1] but most of the work reported has been confined to distribution by molecular weight and chemical class. Only a limited number of investigations has been made on the distribution of the skeletal isomers present. Friedel and Anderson [2] examined the distribution of C_5 to C_8 paraffin isomers from the hydrogenation of carbon monoxide with a cobalt catalyst at 190° C and found that the proportion of branched-chain isomers increased with increase in molecular weight. The results of Weitkamp *et al*,[3] who carried out an exhaustive analysis of product prepared using a fluidized iron catalyst at 315° C indicated that a higher proportion of branched-chain isomers was obtained with iron catalysts; further, these authors concluded that chain structure was insensitive to variations in the reaction conditions.

These and other observations are in agreement with the hypothesis advanced by Herington [4] and elaborated by Anderson, Friedel, and Storch [5] and by Weitkamp,[3] which suggests that the growth of carbon chains in the Fischer–Tropsch synthesis takes place by stepwise addition of a radical containing a single carbon atom to a growing chain adsorbed on the catalyst surface. On this view, the molecular weight distribution of the products is determined by the ratio between the probability that the growing chain will be desorbed from the surface and the probability that it will remain to take part in further growth. The distribution of skeletal isomers is determined by the ratio between the probability of addition of a carbon atom to the end atom of the growing chain and that of addition to the penultimate atom. Since the isomer distribution appeared unaffected by changes in reaction conditions, this latter probability ratio was assumed to be dependent only on the catalyst used.

Macdonald *et al* [6] confirmed that the isomer distribution was different for iron and cobalt catalysts, but showed in addition that, for both types of catalyst, changes in the reaction conditions caused a significant change in the isomer distribution of the C_6 hydrocarbons synthesized. Although other factors could not be entirely excluded, it was concluded that the change in composition was mainly an effect of reaction temperature, the proportion of branched-chain isomers increasing with reaction temperature. The effect observed was not due to secondary isomerization of the initial reaction products. These investigations have been extended in the present work to determine the specific effect of reaction temperature on the isomer distribution of products prepared using an iron catalyst operated at a range of temperatures, but under otherwise identical conditions of pressure, gas composition, etc. The gas space velocity was adjusted to maintain the level of conversion of carbon monoxide and hydrogen approximately constant.

PREPARATION OF SYNTHESIS PRODUCTS

The products were prepared using a reduced iron catalyst (mill scale impregnated with 2 per cent by weight of potassium carbonate and sintered at 850° C) operated with water-gas ($H_2/CO = 1{\cdot}1$) at 20 atmospheres pressure in a small fixed bed reactor.[7]

The temperature range investigated was 200° to 300° C; operation at temperatures above 300° C was prevented by blockage in the catalyst bed. Data have also been included for product prepared at 320° C in a fluidized bed using a similar mill-scale catalyst but with synthesis gas of $H_2/CO = 2{\cdot}0$.[8] Details of the synthesis results, including the distribution of the products into gaseous and non-gaseous hydrocarbons

* MS received 14 March 1958.

† Fuel Research Station, DSIR.

as calculated from the analyses (Bone and Wheeler) of inlet and exit gases, are given in Table I. The boiling range data were obtained by a modified Engler type distillation. The results indicate the expected decrease in the mean molecular weight of the product with increase in reaction temperature.[1] Thus, increase in temperature favours the production of gaseous compounds and increases the proportion of volatile material in the liquid products. A quantitative indication of the extent of this variation is given by the values for the probability factor (α) that a carbon chain will continue to grow rather than be desorbed from the catalyst in accordance with the chain-growth hypothesis developed by Herington[4] and Anderson *et al.*[5] Mean values of α for the products examined have been calculated from the boiling range data by the method suggested by Manes.[9] The plot of α against reaction temperature (Fig 1) shows a regular decrease in α with increase in temperature, although there appears to be no simple relation between the two variables.

TABLE I

Synthesis Data and Boiling Range Distribution of Products

Reaction temperature, ° C	200	230	265	285	300	320 *
Space velocity, vol/vol/hr	75	300	1200	2620	4500	1330
CO-conversion, %	61·0	86·3	84·9	65·3	80·3	97·4
($CO + H_2$)-conversion, %	56·8	75·5	72·2	53·0	67·5	89·6
Usage ratio, H_2/CO	0·93	0·78	0·75	0·74	0·72	1·91
Distribution of products, weight %, methane	1·3	4·8	6·1	8·2	12·3	9·8
C_2–C_4 hydrocarbons	15·5	17·2	19·5	30·8	34·6	32·4
C_{5+} hydrocarbons	83·2	78·0	74·4	61·0	53·1	57·8
Boiling range of liquid product, weight %:						
<50° C	1·3	1·4	11·6	12·7	16·5	70·1
50°–150° C	8·6	9·3	22·8	21·4	33·7	
150°–200° C	5·9	6·4	7·3	12·2	13·2	12·0
200°–250° C	10·1	10·8	8·1	9·5	9·1	8·4
250°–300° C	10·4	11·4	9·1	13·2	9·5	4·8
>300° C	63·7	60·7	41·1	31·0	18·0	4·7
50°–250° C fraction	24·6	26·5	38·2	43·1	56·0	—
Probability of chain growth, α (Manes)[9]	0·930	0·927	0·869	0·859	0·807	0·713

* Product prepared in fluidized bed with gas of $H_2/CO = 2$.

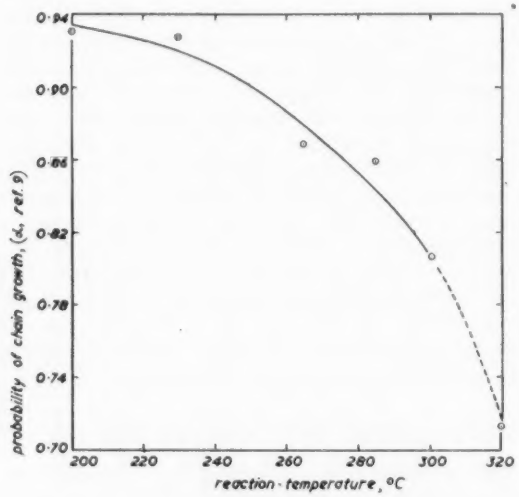

FIG 1

EFFECT OF REACTION TEMPERATURE ON PROBABILITY OF CHAIN GROWTH

ANALYSIS OF PRODUCTS

A combination of modern chromatographic techniques has been applied to analyse the relatively small quantities of products available.

(1) *Liquid Displacement Chromatography*

The method used was based on the fluorescent indicator adsorption method of Ellis and LeTourneau,[10] in which the proportions of paraffinic, olefinic, and aromatic hydrocarbons and total oxygen compounds are determined by introducing the sample (0·8 ml) at the top of a column of silica gel and then adding butylamine as displacing solvent. The components separate during passage down the column, the various interfaces being indicated by suitable fluorescent dyes added to the sample. The proportions of the different classes of compound are determined as percentages by volume by measuring the lengths of the column occupied by them. Determinations on synthetic mixtures verified the validity of the method; if fatty acids were included they did not emerge from the column, so that in all cases this technique provided an analysis of the neutral classes of compound present, and results have been expressed as percentages of total non-acidic material. The maximum proportion of fatty acids present in the original material was about 5 per cent.

(2) *Gas–Liquid Partition Chromatography*

Numerous descriptions of the general technique of gas–liquid partition chromatography have appeared in the literature.[11] The sample (0·01 to 0·05 ml liquid) is dissolved in a non-volatile liquid supported on an inert porous solid packed into a glass tube. On elution with a permanent gas the components of the sample distribute themselves between the liquid and gaseous phases, are separated during passage down the column, and emerge in a well-defined order. Examination of the aliphatic hydrocarbon classes segregated by liquid displacement chromatography, as described above, and collected in a cooled (dry ice) receiver was carried out using a column (6 ft by $\frac{1}{4}$ inch i.d.) with dinonyl phthalate as the non-volatile liquid, kieselguhr as the porous solid (0·4 g ester to 1 g kieselguhr), and nitrogen as eluant. Aromatic hydrocarbons and the fractions containing neutral oxygen compounds required special treatment, which is described later. Detection in all cases was by thermal conductivity cell, and only those fractions boiling below 150° C were investigated. The appara-

tus was essentially the same as that described by Bradford, Harvey, and Chalkley.[12]

Identification of separated components was carried out by determination of the retention time (*i.e.* the time taken for a component to pass through the column) or the corresponding retention volume (volume of carrier gas required to elute a component, corrected for dead space of apparatus and for pressure gradient through the column) which are characteristic of the individual compounds present. Qualitative calibration was accomplished by a combination of direct measurement with pure compounds and utilization of the linear relationship between the number of carbon atoms in a compound and the logarithm of the corresponding retention volume which holds for an homologous series.[12]

Owing to the large number of compounds likely to be present in Fischer–Tropsch product it was decided that complete and definite quantitative calibration by injection of known standard mixtures would not be feasible. Since isomer distribution was the main quantitative objective, it was assumed that equal amounts of isomeric saturated hydrocarbons of a given carbon number would give equal response on the katharometer. This concept of equal response for equal amounts of compounds of the same molecular weight has been claimed by Hausdorff[13] and confirmed to be reasonably accurate for hydrocarbons by Keulemans *et al.*[14] Further, limited verification has been obtained experimentally in this laboratory by analysis of known hexane fractions, and it was considered that the assumption could be extended to the aliphatic pentanes, heptanes, and octanes. Application to aliphatic unsaturated hydrocarbons has also been considered justifiable. Synthetic mixtures were used for calibration prior to the analysis of aromatic hydrocarbons and alcohols. The actual method of quantitative determination was by measurement of the areas of the chromatogram peaks by means of a planimeter. Verticals were dropped from the bottom of peak-to-peak troughs to the base line, where necessary, to allow quantitative measurement between peaks that were not fully separated.[15] Proportions of paraffin and olefin isomers have been recorded as percentages by volume. The differences in density between the isomers are sufficiently small for the values to be read as percentages by weight within the experimental error of the analytical procedure.

COMPOSITION OF PRODUCTS

(1) *Distribution of Chemical Classes*

The results showing the product distribution by chemical type obtained when the individual distillation fractions were submitted to fluorescent indicator adsorption analysis are shown in Table II. Also included in this table are the results for a wide (50°–250° C) fraction obtained both by calculation from the data for the narrower fractions and by single determinations on recombined fractions. The agreement between the results indicates that a single wide fraction gives an accurate mean analysis. Of the

TABLE II

Analysis of Products by Displacement Chromatography

(per cent by volume)

Reaction temperature, ° C	Distillation fractions, ° C	50–150	150–200	200–250	250–300	50–250	
						Calculated	Found
200	Neutral oxygen compounds	18·1	20·4	17·2	21·6	18·3	21·5
	Aromatic hydrocarbons	0·5	2·0	2·6	2·5	2·0	1·7
	Unsaturated hydrocarbons	60·6	56·7	57·2	55·8	58·0	56·7
	Saturated hydrocarbons	20·8	20·9	23·0	20·1	21·7	20·1
230	Neutral oxygen compounds	18·7	20·2	18·9	17·8	19·1	18·7
	Aromatic hydrocarbons	1·5	1·9	3·6	2·4	2·5	2·3
	Unsaturated hydrocarbons	60·1	56·9	54·3	52·1	57·0	58·7
	Saturated hydrocarbons	19·7	21·0	23·2	27·7	21·4	20·3
265	Neutral oxygen compounds	14·7	16·1	14·7	15·8	15·0	14·9
	Aromatic hydrocarbons	0·5	3·4	3·2	3·7	1·6	2·1
	Unsaturated hydrocarbons	69·1	63·6	63·7	62·2	67·2	67·6
	Saturated hydrocarbons	15·7	16·9	18·4	18·3	16·2	15·4
285	Neutral oxygen compounds	17·6	8·0	11·7	9·0	13·6	12·0
	Aromatic hydrocarbons	1·5	3·0	4·0	6·1	2·5	2·8
	Unsaturated hydrocarbons	63·9	65·7	58·5	58·8	63·2	64·4
	Saturated hydrocarbons	17·0	23·3	25·8	26·1	20·7	20·8
300	Neutral oxygen compounds	7·1	7·5	9·2	8·9	7·5	8·7
	Aromatic hydrocarbons	2·4	5·0	6·9	7·6	3·8	4·2
	Unsaturated hydrocarbons	71·8	65·5	61·8	63·3	68·7	68·0
	Saturated hydrocarbons	18·7	22·0	22·1	20·2	20·0	19·1

T

classes of compound present, the proportion of saturated hydrocarbons remained substantially unchanged, but the proportions of aromatic and unsaturated hydrocarbons increased with increase in reaction temperature, while the content of compounds containing oxygen decreased. The results for the fractions of narrow boiling range from product prepared at a given reaction temperature indicate that the proportion of aromatic hydrocarbons increased and that of unsaturated hydrocarbons decreased with increase in molecular weight.

(2) *Distribution of Structural Isomers in Hydrocarbon Fractions*

(*a*) *Saturated Hydrocarbons.* The individual saturated fractions separated from the other classes by liquid displacement chromatography were analysed

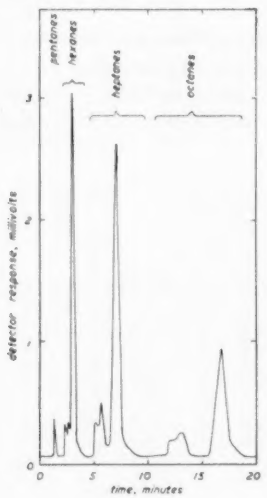

FIG 2

CHROMATOGRAM–PARAFFIN FRACTION

by gas–liquid partition chromatography. The dinonyl phthalate column used was operated at an outlet pressure of 24 cm of mercury and 45° C for the fraction boiling below 50° C containing *n*- and *iso*-pentane, and at 60° C for the fraction boiling between 50°–150° C containing the C_6, C_7, and C_8 isomers. The flow rate of nitrogen was 20 ml per minute.

Fig 2 shows a typical chromatogram obtained from a saturated hydrocarbon fraction. In each case the branched-chain isomers precede the corresponding straight-chain compound. In only one case, that of the hexane fraction in the product prepared at a reaction temperature of 230° C, was the separation between the peaks for the *n*-paraffin and the 2- and 3-methyl isomers inadequate for reliable quantitative analysis. The data (Table III) for this fraction have not been used in estimating the extent of chain-branching in the product concerned. There was no evidence of any appreciable amounts of naphthenes

TABLE III

Isomer Distribution of C_5 *to* C_8 *Paraffin Hydrocarbons*

(per cent by volume)

Reaction temperature, ° C	200	230	265	285	300	320 †
2-Methylbutane	7·0	8·2	9·7	10·5	11·6	—
Pentane	93·0	91·8	90·3	89·5	88·4	—
2-Methylpentane	5·7	7·6	7·6	7·4	7·1	—
2,3-Dimethylbutane						
3-Methylpentane	4·7		6·0	7·3	7·9	—
Hexane	89·6	92·4	86·4	85·3	85·0	—
2-Methylhexane	5·5	6·2	5·4	6·7	7·1	32·1
2,3-Dimethylpentane						
3-Methylhexane	7·7	9·2	13·5	12·2	15·1	
Heptane	86·8	84·6	81·1	81·1	77·8	67·9
2-Methylheptane	7·0	6·9	8·2	11·2	11·5	38·6
2,3-Dimethylhexane						
3-Methylheptane	9·2	9·9	11·5	13·3	17·1	
4-Methylheptane						
Octane	83·8	83·2	80·3	75·5	71·4	61·4
Probability factor "A" from:						
Pentanes	0·064	0·958	0·950	0·946	0·940	—
Hexanes	0·964	0·974	0·952	0·948	0·947	—
Heptanes	0·965	0·959	0·949	0·949	0·939	0·908
Octanes	0·965	0·964	0·957	0·945	0·935	0·907
Mean	0·965	0·960 *	0·952	0·947	0·940	

* Omitting hexanes.
† Product prepared in fluidized bed with gas of $H_2/CO = 2$.

which could interfere with the paraffins of next higher carbon number. The compounds identified were: 2-methylbutane and *n*-pentane from the fraction boiling below 50° C, branched hexanes, *n*-hexane, branched heptanes, *n*-heptane, branched octanes, and *n*-octane from the higher boiling fraction as indicated in Table III, which includes the proportion of straight-chain compound found in fractions of individual carbon number (C_5 to C_8) for the five reaction temperatures.

For each of the products investigated the proportion of *n*-isomer decreases with increase in carbon number. Anderson, Friedel, and Storch [5] showed that the observed distribution of skeletal isomers could be predicted by assuming that addition of a further carbon atom to the end or the penultimate carbon atom of a growing chain took place according to a fixed ratio of probabilities. If the probability of addition to the end carbon atom is denoted by A and it is assumed that for any one product A is independent of chain length and branching, the molar proportion of the *n*-isomer of carbon number N is related to A by the expression

$$A = \frac{\text{Proportion of } n\text{-}C_{N+1}}{\text{Proportion of } n\text{-}C_N} \quad . \quad (1)$$

or more reliably by

$$\text{Molar proportion } n\text{-}C_N = A^{N-3} \quad . \quad (2)$$

Values calculated by equation (2) for the fractions of different carbon number investigated are given in Table III; for product prepared at any one reaction

temperature the probability factor is substantially constant in agreement with the observations of Anderson *et al.*[5] A plot (Fig 3) of the *n*-isomer content on

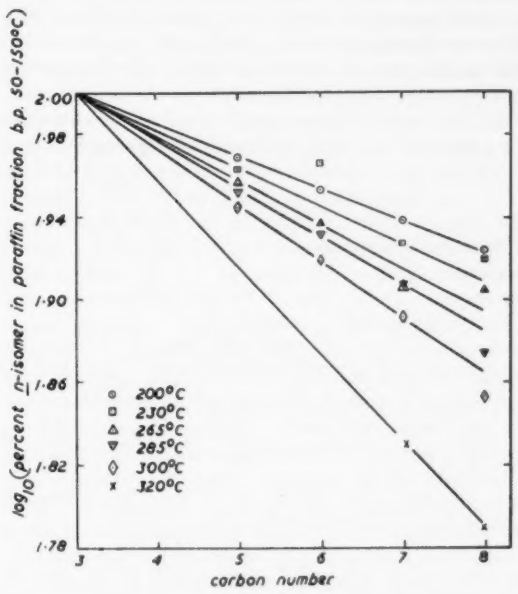

FIG 3

VARIATION IN PROPORTION OF *n*-ISOMER WITH CARBON NUMBER: PARAFFIN HYDROCARBONS

a logarithmic scale against carbon number confirms the linear relation reported by Weitkamp *et al* [3] and the conclusion that growth of carbon chains during synthesis occurs at one end of the chain only.

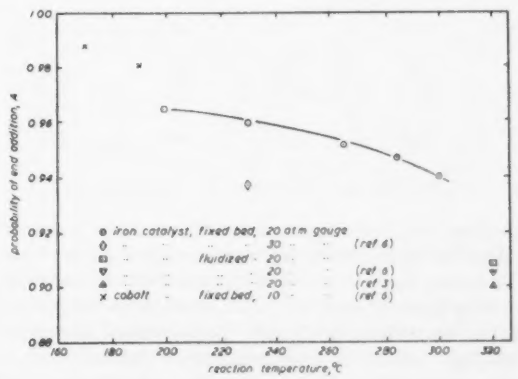

FIG 4

PROBABILITY OF CHAIN-BRANCHING AS A FUNCTION OF TEMPERATURE

It is evident, however, from the data in Table III that the proportion of *n*-isomer present in a fraction of given carbon number decreases with increase in reaction temperature. Correspondingly, the values of the probability factor *A* decrease in a regular manner with increase in reaction temperature, as is indicated in Fig 4. Although the relation between *A* and reaction temperature does not appear to be a simple one, all the points for a mill-scale catalyst operated in a fixed bed at 20 atm with water-gas lie on a smooth curve. Values of *A* calculated from the data of Macdonald *et al* [6] have been included; that for product prepared with a mill-scale catalyst operated in a fluidized bed at 320° C and 20 atm pressure of synthesis gas ($H_2/CO = 2$) approximates to the curve. The value of *A* (0·907) obtained by these authors using a combination of fractional distillation and infra-red spectrometry is in excellent agreement with the value ($A = 0{\cdot}908$) determined in the present work by chromatographic analysis for a similar product prepared using the same catalyst, and with the value ($A = 0{\cdot}90$) reported by Weitkamp.[3]

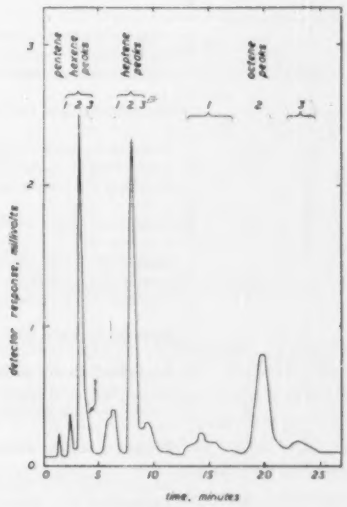

FIG 5

CHROMATOGRAM–OLEFIN FRACTION

(*b*) *Unsaturated Hydrocarbons.* For analysis of the unsaturated hydrocarbons by gas–liquid partition chromatography the same operating conditions were used as for the paraffin fractions, and the same carbon number fractions (C_5 to C_8) were investigated. Interpretation of the chromatograms, of which a typical example is given in Fig 5, proved more complicated because of the increase in the number of components arising from the presence of skeletal, positional, and geometric isomers.

In general, the chromatograms obtained for the olefin fractions exhibited three main peaks or groups of peaks for each carbon number. Comparison of experimental chromatographic data for a number of reference compounds, in conjunction with the work of Sullivan *et al*,[16] indicated that the largest peak (*e.g.*

Peak 2, Fig 5) corresponded to the straight-chain α-olefins but included also the 2-methyl-α-isomers. Peak 1 corresponded to the branched-chain olefins (predominantly α-olefins but excluding the 2-methyl-α-olefins), and the third peak, which in some instances was represented only by a shoulder on the main peak, indicated the presence of *n*-olefins with internal double bonds.

It is apparent from Table IV that the main components present are the straight-chain α-olefins, but that the proportions of branched-chain olefins and of internally unsaturated olefins increase with increase in molecular weight. Further, for the fractions of any given carbon number, the proportions of branched-chain isomers increase with reaction temperature. The data obtained for the olefins are less susceptible to mathematical treatment than those for the paraffins, and consistent values for the probability of end addition to the carbon chain are not available directly. Calculation of the proportions of branched-chain olefins, excluding the 2-methyl-α-olefins, using the probability factor derived for the corresponding paraffinic fractions, however, gives values which are in good agreement with those observed (Table IV). There is therefore strong presumptive evidence that the mechanism of growth is similar for the olefinic and paraffinic hydrocarbons.*

(*c*) *Aromatic Hydrocarbons.* Because of the small amounts of aromatic hydrocarbons present it was decided to investigate only those from products obtained at the three highest reaction temperatures. To ensure that a representative analysis was obtained, two samples of each aromatic fraction were collected after separation by liquid displacement chromatography. In one of these an accurate cut was made on the adsorption column between unsaturated and aromatic hydrocarbons and the boundary between aromatic hydrocarbons and oxygen compounds pur-

TABLE IV

Isomer Distribution of C_5 *to* C_8 *Unsaturated Hydrocarbons*

(per cent by volume)

Synthesis temperature, °C	Peak number	Peak identity	Carbon number			
			5	6	7	8
200	1	Branched-chain olefins	3·8	6·7	9·9	11·9
	2	*n*-α-olefins + 2-methyl-α-olefins	96·2	93·3	85·2	83·0
	3	*n*-olefins with internal unsaturation			4·9	5·1
	1	Branched-chain olefins (calculated)	3·4	6·7	9·7	12·6
230	1	Branched-chain olefins	—	7·7	11·0	11·0
	2	*n*-α-olefins + 2-methyl-α-olefins	—	92·3	82·3	80·7
	3	*n*-olefins with internal unsaturation	—		6·7	8·3
	1	Branched-chain olefins (calculated)	—	6·9	10·2	12·8
265	1	Branched-chain olefins	4·8	8·1	13·1	14·3
	2	*n*-α-olefins + 2-methyl-α-olefins	95·2	91·9	79·3	78·6
	3	*n*-olefins with internal unsaturation			7·6	7·1
	1	Branched-chain olefins (calculated)	4·4	8·2	12·7	15·0
285	1	Branched-chain olefins	4·8	9·1	15·8	17·3
	2	*n*-α-olefins + 2-methyl-α-olefins	95·2	90·9	72·4	73·1
	3	*n*-olefins with internal unsaturation			11·8	9·6
	1	Branched-chain olefins (calculated)	5·3	9·8	15·3	17·6
300	1	Branched-chain olefins	6·2	10·2	18·2	18·7
	2	*n*-α-olefins + 2-methyl-α-olefins	93·8	89·8	66·7	64·3
	3	*n*-olefins with internal unsaturation			15·1	17·0
	1	Branched-chain olefins (calculated)	6·4	11·4	18·1	20·0

* Since this paper was written catalytic hydrogenation of olefin fractions (0·02 ml sample) and analysis of the paraffins formed has been carried out by inserting a hydrogenation reactor between the sample injection point and the chromatographic column and using hydrogen as eluant (*cf.* Emmett *et al. J. Amer. Chem. Soc.*, 1955, **77**, 5860). Results obtained confirm the conclusion that the distribution of skeletal isomers, and therefore the mechanism of growth, are identical for paraffins and olefins.

posely over-run to increase the volume of material, and in the other an accurate cut was made at the aromatic hydrocarbon–oxygen compound boundary, a small volume of unsaturated hydrocarbon having previously been collected with the aromatic portion.

The fractions containing some oxygen compounds were analysed chromatographically on a dinonyl phthalate column operated at 72° C. Benzene, toluene, ethylbenzene, *m*- + *p*-xylenes, and *o*-xylene were detected and determined, but both the benzene and the *o*-xylene peaks were affected by oxygen compounds. The other fractions were analysed on a chromatographic column packed with 1 part by weight of kieselguhr to 0·4 part by weight of a polyethylene glycol of average molecular weight 200 and operated at 70° C and 40 cm of mercury outlet pressure. This stationary phase retards the aromatic hydrocarbons relative to the unsaturated hydrocarbons, allowing the detection and determination of benzene, toluene, and *o*-xylene, but does not give adequate separation of ethylbenzene from *m*- and *p*-xylenes. No separation of *m*- from *p*-xylene was obtained with any variation of the chromatographic technique investigated. In all cases the benzene peak coincided with that of a contaminant which is believed to be a C_{10} aliphatic hydrocarbon. This rendered it difficult to calculate completely the distribution of the aromatic hydrocarbons identified. The proportions by volume of the C_6 and C_8 aromatics have therefore been expressed in Table V relative to the amounts of toluene; values for benzene are subject to an error of about 10 per cent.

TABLE V

Distribution of Aromatic Hydrocarbons

Synthesis temperature, ° C	265	285	300	320 *
Benzene . . .	0·28	—	0·38	—
Toluene . . .	1·00	1·00	1·00	1·00
Ethylbenzene . . .	0·31	0·30	0·32	0·23
o-Xylene . . .	0·39	0·31	0·32	0·13
m- + *p*-Xylenes . .	0·24	0·24	0·25	0·14

* Product prepared in fluidized bed with gas of $H_2/CO = 2$.

Of the individual aromatic hydrocarbons the highest yield was recorded for toluene.

The data available for the distribution of the C_8 aromatic hydrocarbons (Table VI) agree with those of Weitkamp[3] in showing that the relative proportions of isomers present deviate widely from those demanded by thermodynamic equilibrium.[17] This divergence favours the hypothesis[3] that aromatic hydrocarbons are formed by ring closure between the growing end of the carbon atom chain on the catalyst surface and a carbon atom already present in the chain. On this hypothesis *m*- and *p*-xylene can be formed only from branched C_8 chains. Ethylbenzene and *o*-xylene can arise from suitably branched chains, but their most probable mode of formation is by cyclization of straight C_8 chains, ethylbenzene by 1–6 linkage, and *o*-xylene by 2–7 linkage. By consideration of the possible ring closures in conjunction with the distribution of the skeletal isomers of the C_8 and C_9 aliphatic hydrocarbons, Weitkamp[3] developed a scheme which predicted the distribution of the C_8 and, less successfully, the C_9 aromatic hydrocarbons in a product prepared using a fluidized iron catalyst.

The data obtained in the present study are not considered adequate to assess fully the value of this prediction scheme. There is, however, qualitative agreement between the relative proportions of *m*- + *p*-xylene and *o*-xylene + ethylbenzene and those of the *iso*- and *n*-C_8 paraffins respectively (Tables VI and III).

With increase in the reaction temperature from 265° to 300° C the proportion of ethylbenzene increases and that of *o*-xylene decreases. Comparison with data obtained at 320° C under fluidized-bed conditions, which are in good agreement with the results reported by Weitkamp, confirm this trend.

It would appear therefore that with increase in reaction temperature the rate of ring closure involving the terminal carbon atom of the growing chain increases relative to the rate of closure via the penultimate carbon atom.

TABLE VI

Isomer Distribution of C_8 Aromatic Hydrocarbons

(mol per cent)

Synthesis temperature, ° C	265	285	300	320 *	Weitkamp[3] 315	Thermodynamic equilibrium[17] at 227° C	Thermodynamic equilibrium[17] at 327° C
Ethylbenzene .	23·1	35·2	36·3	45·8	46	3·7	5·9
o-Xylene .	41·2	36·8	35·7	25·9	29	20·4	21·6
m- + *p*-Xylene .	25·7	28·0	28·0	28·3	25	75·9	72·5

* Product prepared in fluidized bed with gas of $H_2/CO = 2$.

(3) *Distribution of Alcohols*

Since they are soluble in water, the lower-boiling oxygen compounds formed in the synthesis are distributed between the oil and water layers in the product. Identification and determination of the alcohols boiling in the range 50° to 150° C therefore involved examination of the reaction water, the oil product boiling below 50° C, which contains alcohols due to azeotrope formation, and of the oxygen compounds separated by displacement chromatography from the oil boiling from 50° to 150° C.

Gas–liquid partition chromatographic analysis of the oxygen compounds boiling from 50° to 150° C, using glycerol as the stationary phase at 60° C and 40 cm of mercury outlet pressure, gave complete

separation of the alcohols from the carbonyl compounds and esters present. The alcohols themselves, however, were not completely resolved; although adequate separation of *iso*propanol, propanol, secondary butanol, and pentanol was obtained, *iso*butanol coincided with ethanol and the methyl butanols with butanol. A second sample of the 50° to 150° C spirit was therefore shaken with Amberlite resin IRA 400 in the bisulphite form to remove the carbonyl compounds, and the remaining oxygen compounds, after separation from the hydrocarbons on a silica gel adsorption column, were analysed using a dinonyl phthalate column at 72° C and 40 cm of mercury outlet pressure. Since traces of water and ethanol were introduced during the bisulphite treatment, quantitative analysis by this procedure was confined to alcohols boiling above *iso*propanol. Combination of the results from the two procedures, however, gave sufficient information for complete analysis of the alcohols in the 50° to 150° C spirit fraction. Determination of ethanol and methanol in the oil boiling below 50° C was carried out by analysis of the whole fraction on glycerol and polyethylene glycol columns at 60° C. For analysis of the alcohols in the aqueous product, the neutralized reaction water was saturated with potassium carbonate, extracted with ether, and the ether extract evaporated to remove solvent. The resulting mixture of oxygen compounds was subjected to gas–liquid partition chromatographic analysis using a dinonyl phthalate column at 72° C and outlet pressure 40 cm of mercury and a column of polyethylene glycol (average molecular weight 400) operated at 62° C and 40 cm of mercury outlet pressure. Combination of the results obtained was required for a complete analysis of the alcohols present.

TABLE VII

Distribution of C_1 *to* C_5 *Alcohols*

Reaction temperature, ° C	265	285	300	320 [a]	
Alcohol:					
Weight % of C_1–C_5 alcohols—					
Methanol	0·6	0·8	0·8	1·6	
Ethanol	46·7	42·3	62·1	55·0	
Propanol-2	0·6	0·8	0·6	1·3	
Propanol-1	18·6	17·8	14·0	15·1	
2-Methyl propanol-1	1·3	1·4	1·0	3·0	
Butanol-2	1·2	1·0	1·2	5·6	
Butanol-1	9·6	11·3	6·5	7·8	
Total methyl butan-1-ols	2·5	3·0	2·3	4·0	
Pentanol-2 + pentanol-3	1·5	2·5	1·4	2·2	
Pentanol-1	17·4	19·1	10·1	4·4	
Mol % of C_1–C_5 alcohols—					Weitkamp [3]
Methanol	1·1	1·5	1·3	2·7	0·6
Ethanol	57·6	53·5	71·4	64·3	59·4
Propanols	18·2	18·0	12·8	14·7	27·0
Butanols	9·3	10·8	6·2	11·9	8·7
Pentanols	13·8	16·2	8·3	6·4	4·3

[a] Product prepared in fluidized bed with gas of $H_2/CO = 2$.

The proportions of C_1 to C_5 alcohols present in the total aqueous and non-aqueous product analysed are tabulated in Table VII.

A small amount of methanol was identified, but the main alcohol present was ethanol in all cases. For each product the molar proportions of the C_2, C_3, and C_4 alcohols decrease regularly with increase in molecular weight, but the proportion of pentanols is higher than that of the butanols. This latter observation, which does not appear to arise from experimental error, disagrees with the results obtained for product prepared with a fluidized mill-scale catalyst operated at 320° C with gas of $H_2/CO = 2$. These latter results agree with data reported by other workers.[3, 18] It may, however, be significant that a similar anomaly was observed in the distribution of the alcohols obtained by synthesis using a cobalt catalyst.[19] In this case an abnormally high proportion of butanol was found which was correlated with the higher stability of butanol under the synthesis conditions used.

The distribution of isomers in the C_3 to C_5 alcohols is given in Table VIII. The major component in each

TABLE VIII

Isomer Distribution of C_3 *to* C_5 *Alcohols*

Synthesis temperature, ° C	265	285	300	320 [a]
Distribution, mol %:				
Skeletal isomers—				
Straight-chain butanols/total butanols	89·3	89·8	88·5	81·7
Straight-chain pentanols/total pentanols	88·3	87·8	83·3	62·2
Probability factor A				
From butanols	0·893	0·898	0·885	0·817
From pentanols	0·940	0·937	0·912	0·788
From paraffin hydrocarbons	0·952	0·947	0·940	0·908
Substitutional isomers—				
Propanol-1/total propanols	96·9	95·7	95·9	92·1
Butanol-1/total straight-chain butanols	88·9	91·9	84·4	58·2
Pentanol-1/total straight-chain pentanols	92·1	88·4	87·8	66·7

[a] Product prepared in fluidized bed with gas of $H_2/CO = 2$.

case is the straight-chain primary alcohol, but the proportion present decreases with increase in molecular weight for any one product. For a fraction of given carbon number the results confirm those observed for the hydrocarbons in showing a decrease in the proportion of straight-chain isomer with increase in the synthesis temperature. The probability factor for end addition thus decreases with increase in temperature, but the values obtained appear to be lower than those found for the paraffin hydrocarbons. This difference was not observed by Weitkamp,[3] who drew attention to the similarity between the distributions of the alcohols and hydrocarbons. The probability factor also appears to vary with carbon number, and the proportion of straight-chain butanols is unexpectedly low. These observations may reflect differences between the manner of growth of alcohols and hydrocarbons on the catalyst surface or in the desorption reactions by which these compounds are formed from a common precursor. It is considered, however, that the differences are more likely to arise from the different stabilities of the individual alcohols.

Thus, it has been shown for cobalt [19–21] and

iron [22] catalysts that the proportions of individual alcohols in the synthesis products are controlled by their rates of decomposition under the operating conditions. Data for the iron catalyst used in the present investigation are not available, but the relative decomposition rates on a cobalt catalyst [20] of butanol-1, *iso*butanol, and butanol-2 have been shown to be as 60 : 46 : 87, so that decomposition of the straight-chain isomers occurs preferentially. Since the main products formed are hydrocarbons, the difference in skeletal distribution between hydrocarbons and alcohols in a given synthesis product will increase with the extent of decomposition of the alcohols, *e.g.* with increase in operating temperature. Some evidence of this trend is apparent from the data in Table VIII.

Although the differences are small, there appears to be a tendency for the proportions of primary alcohols to decrease with increase in the synthesis temperature. This trend may be of interest in view of the observations of Kummer and Emmett [23] that, when radioactive alcohols are incorporated in the synthesis on iron catalysts at atmospheric pressure and 230° C, the position of the hydroxyl group defines the point of attachment of the next carbon atom. Thus the C_4 hydrocarbons obtained from *n*-propanol were almost exclusively straight-chain and those from *iso*propanol branched-chain. If re-incorporation of alcohols occurs during synthesis, a decrease in the proportion of primary alcohols formed initially may lead to an increased production of branched-chain compounds.

The change in the proportion of primary alcohols may also have some significance in relation to the increased production of internally unsaturated olefins observed at high reaction temperatures. In view of the probability that migration of double bonds occurs under synthesis conditions, however, the establishment of a quantitative correlation between the distribution of positional isomers in the alcohols and olefins would appear unlikely.

CONCLUSIONS

The temperature of the synthesis reaction has a profound influence on the composition of the liquid products of the Fischer–Tropsch process. With increase in temperature in the range 200° to 300° C the mean molecular weight of the product falls. The probability factor for chain growth on the catalyst surface, which has been suggested by Manes [9] as a suitable parameter for assessing variation in boiling-range distribution, decreases regularly with increase in temperature, although no simple quantitative relation has been found.

As reaction temperature increases the proportion of oxygen compounds present decreases in favour of olefinic and aromatic hydrocarbons. This trend confirms results already reported and is in agreement with the hypothesis [19] that oxygen compounds, specifically alcohols, are the precursors of hydrocarbons in the synthesis and that the proportion of alcohols present is determined by their stability under the operating conditions.

Examination of the distribution of skeletal isomers has confirmed for paraffins, olefins, and alcohols that the proportion of branched-chain isomers in a given product increases with increase in carbon number. The data support the hypothesis [2,5] that isomer distribution is controlled by a constant ratio of the probabilities of addition of a radical containing a single carbon atom to the terminal or to the penultimate carbon atom of the growing chain.

It has been generally accepted that this probability ratio, and consequently the distribution of skeletal isomers, was characteristic of the synthesis catalyst and was insensitive to changes in operating conditions. The present investigation, however, confirms and extends the work of Macdonald, Sweett, and Hall [6] in demonstrating that isomer distribution is sensitive to variation in the reaction temperature, the proportion of branched-chain isomers increasing with temperature. With the iron catalyst used the magnitude of the change in the probability ratio (*A*, Fig 4) is considerable, the observed value ranging from 0·965 at 200° C to 0·940 at 300° C. These values are intermediate between those reported for cobalt catalysts operated at temperatures below 200° C (0·96 to 0·99) [24] and for iron catalysts operated at temperatures above 300° C (0·91) [3, 6]. It would appear therefore that the difference in isomer distribution between products from iron and cobalt catalysts respectively is controlled to a major extent by the different reaction temperatures at which these catalysts are operated.

The divergence from the present results of the value for this probability ratio calculated for a mill-scale catalyst operated at 230° C from the data of Macdonald *et al* [6] (Fig 4) suggests that variables other than reaction temperature can influence isomer distribution. A study of the effect of other variables is in progress: from the examination of products obtained with an iron catalyst operated in a slurry system it appears that isomer distribution is not sensitive to operating pressure in the range 10 to 30 atmospheres, or to variation in the level of conversion.

ACKNOWLEDGMENTS

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HYDROCARBONS FROM PETROLEUM *

By FREDERICK D. ROSSINI

DISCUSSION †

Professor E. S. Sellers: Dr Rossini did not mention his very valuable work of obtaining the thermodynamic properties of the hydrocarbons he has isolated, and he is perhaps better known for this aspect of API Research Project 6 than for anything else. Like many others, I was struck by the constancy of the ratio of the individual chemical compounds within their respective classes. Has Dr Rossini ever examined whether this distribution represents an equilibrium mixture in the chemical thermodynamic sense?

Dr F. D. Rossini: Some calculations were made about thirteen years ago on this problem, particularly as regards the branched hexanes and the C_8 alkyl benzenes. It was found that if the relative amounts of the branched hexanes are taken as they occur in the liquid state in the petroleum in the ground, and the thermodynamic equilibrium of those same isomers calculated, the chemical thermodynamic equilibrium corresponds to that of the gas phase at about 300° C. Within the limits of the calculations, this is the same for the branched hexanes and the C_8 alkyl benzenes, in each group. The work has not been pursued, and a lot more information is needed, because it has been said by a number of people that the petroleum could never have been subjected to any such high temperature.

Dr C. A. Finch: Have you discussed this constancy of ratio in terms of the geological origin of the petroleum?

Dr F. D. Rossini: Here again the extent of the information available is not yet enough to enable us to make very strong conclusions. Dr Harold Smith of the U.S. Bureau of Mines and possibly others have made calculations along these lines, but more information on the geological side of the problem is needed.

Dr A. A. L. Challis: Have you used vapour phase chromatography in the more recent parts of your work?

Dr F. D. Rossini: Vapour phase chromatography has not been employed, because of the fact that while the quantities handled are relatively small compared to industrial laboratory operation, they are still much larger than can be handled in any convenient sort of way in any operation that would involve vapour phase adsorption or chromatography. Four or five years ago a calculation was made of the size of apparatus that would be needed to process some of our quantities of material, and it turned out to be much beyond us.

For example, in processing by adsorption in the liquid phase, several steel columns which are 70 feet tall and 2 inches in diameter have to be used.

There is a great use and benefit from vapour phase operation for analytical purposes in certain later stages of the work, and in certain cases where it is desired to know something about the complexity of certain final fractions in which there might be a small number of constituents.

Dr L. K. Beach: In all the crude oils studied, the individual components in the paraffinic class have a close numerical relationship one to another. The aromatic components similarly have within limits a fixed relationship one to another, and the naphthenics also. Yet from crude to crude the ratios of paraffins to aromatics to naphthenes vary considerably. Could this not be due to the fact that in the community of living matter which gave rise to the crudes, the paraffins came predominantly (and the aromatics and naphthenes, to a minor extent) from one type or class of living matter such as animals; likewise, the aromatics predominantly from another class of living matter, such as trees, and the naphthenics predominantly from still another class, such as aquatic life? In a given crude oil one would expect a variation in the ratios of paraffins to aromatics to naphthenes, depending on the types of life dominant in the region, or regions, in which that crude was laid down or formed.

If terrestrial animals, for example, predominated as the source of a given crude oil, then that portion of the oil arising from the decomposition of these animals would reasonably be expected to be similar in its composition to that arising from animals in a region where plants or other life predominated.

Following this train of thought, it would seem that the current studies of the types of porphyrins in crude oil might give us some answers as to what type of life, as judged by porphyrin type, gave rise to what class of oil components.

Dr F. D. Rossini: I think that the comments made indicate why I am a little hesitant in making any conclusions. I am glad, for another reason, that you raised this point. Another important comment which I should have made relates to the tying in of the results of the exhaustive analysis of one representative petroleum with the more abbreviated observations made on the other gasoline fractions. One can take any given petroleum and make certain rather routine observations on it, and obtain some figures that permit translation of the findings on this one representative petroleum over to the unknown petroleum, at least as to the magnitude of the amounts, and perhaps even much closer than could be measured without a great deal of effort.

C. S. Windebank: There were three points about the crude used as a basis for this work which must have interested many people.

First of all, it is rather more volatile than usual; secondly, it is remarkably low in sulphur; and thirdly, it is no longer in production.

Can Dr Rossini say whether he, or for that matter the API, has under consideration another such thorough study based on a crude which is of commercial interest,

* See pages 97–107. † This discussion followed the reading of the paper on 9 July 1957.

and, in particular, one which contains the impurities, particularly sulphur, which cause so much trouble today? This would involve a challenge to our analytical methods, but probably no greater a challenge than was the case with the work now described when it was started.

Dr F. D. Rossini: This gives me an opportunity to mention something about several other API Research Projects which have been established to obtain some of the information mentioned.

Several years ago the API established Research Project 48 for the sole purpose of investigating the composition of the sulphur compounds in petroleum. This project has made good progress.

The API has also started a sister project, API Research Project 52, on nitrogen compounds in petroleum.

To come back to the observation on this representative petroleum, it is definitely true that this was low in the lubricant fraction. In a way, maybe fortuitously, this was fortunate, because it gave us more of the lower material to work on. About 20 years ago, the Project did start an investigation on a large quantity of another lubricant fraction, but it was abandoned after two or three years. I should at this point again emphasize that I have been talking only about the work of our laboratory. A number of laboratories and many people have been working on the composition of petroleum with certain specific things in mind. All that we have learned from that work has tended to confirm the ideas that we have developed with respect to the composition of this one petroleum and of other petroleums.

The final point is that even if we had a large quantity of the lubricant fraction, about all we could learn about it would be what most other laboratories could learn about it, perhaps even more quickly than we could, namely by size and type analysis.

In our strivings to try to get down to the individual compounds we have found that it is very helpful to work up from the lower ranges, because we can keep predicting ahead step by step and can extrapolate safely.

L. D. Miskin: As far as lubricating oils are concerned, the molecular weight is so high that a little sulphur goes a long way. I wonder if there are any hydrocarbons in certain lubricating oils because of that.

Dr F. D. Rossini: That is quite correct. Even for what one might call a very low sulphur material, a sulphur atom carries with it a lot of carbons and hydrogens. A short time ago I made some calculations, and your observations are quite correct. I am not sure that I would go so far as to say there are no pure hydrocarbons there, but at least let us say that a large quantity of carbon and hydrogen is tied up in molecules containing sulphur.

C. B. Milne: I think that, in API Research Project 48, a method of thermal diffusion was used for separating various structures of different kinds of molecules. Have you had any experience with this?

Dr F. D. Rossini: With respect to fractionating processes in general, our needs are quite particular and specific, and many processes which are found most useful in other laboratories are not very useful to us. One of the reasons is that we are faced with a mixture of unknown molecules of different sizes and different types. We would like to have fractionating processes that do things that we know they are going to do with respect to the size of molecules, on the one hand, or the type of molecules, on the other. So we come to a fractionating process that may separate by reason of size or shape of molecule, independent of its type. This would be a process that would be useful to us only at the very end when we have a rather simple fraction, because it will not do us any good to take the original material and separate it into a lot of mixtures which are still complex in a way that is not known to us. All that does is to provide for us many more fractions to operate on our regular procedures. So for our work, we class thermal diffusion with crystallization.

Dr S. F. Birch: In using molecular sieves, have you had much trouble in recovering hydrocarbons afterwards?

Dr F. D. Rossini: Yes.

H. C. Rampton: I would like to ask about silica gel supplies. I presume that Davison has been used throughout. In view of the high cost, is the desorbent regenerated for re-use? As some silica gels offered in the U.K. have been found to be slightly acid, difficulty has been encountered with formation of small quantities of acid tar, due to the relatively high desorbate ratio employed. Have you experienced similar trouble or are the Davison grades so good that they analyse better than 99·99 per cent silica?

Dr F. D. Rossini: At the beginning of our work we did have difficulty, but we prevailed upon the Davison Chemical Company to supply us with what one might call clean material, suitable for the needs of our work.

When we set up the 70-foot columns mentioned, we thought also of regenerating in position, and actually tried that several times. We calculated the cost and, for our purposes, it was more economical to use new material.

A NEW APPARATUS FOR THE DETERMINATION OF OCTANE NUMBERS ON SMALL SAMPLES *

By D. B. CHITTY †

THE determination of a single CFR Motor or Research Method octane number by the Standard Method [1] requires approximately 400 ml of fuel. To obtain this quantity in research work, small pilot plants must often be run for long periods, with resultant high cost. Consequently there has been much development work in Britain and the U.S.A. into methods requiring much less than 400 ml of sample for determining octane number, while maintaining the same accuracy as the Standard Methods. With the two suggested published methods,[2] it has been found that any attempt to reduce the sample quantity below 100 ml has often resulted in a drop in accuracy of rating compared with standard methods. These two published methods achieve a saving in fuel by eliminating, or drastically reducing, the fuel held up in the carburettor float

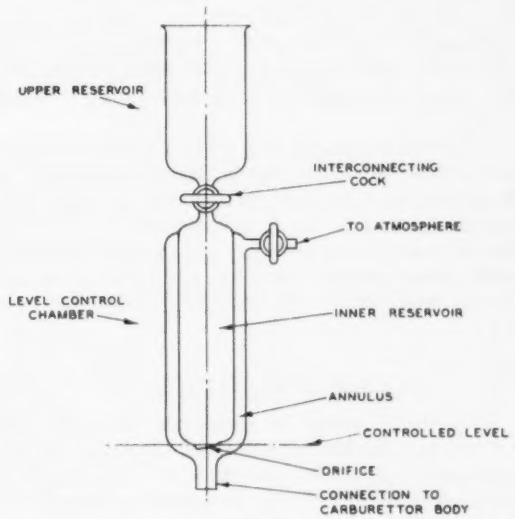


FIG 1

chamber; this normally accounts for some 100 ml. However, in the method using the small float bowl fuel system, which is generally considered the more reliable of the two methods, no attempt is made to save fuel during the engine stabilization time after changing from reference to test fuel; this accounts for approximately 40 ml during a full test on very sensitive fuels. The usual procedure during this period is to enrich the mixture strength of the sample beyond the maximum knock level before switching over from the reference fuel; after the stabilization of knock, the mixture strength is weakened in increments until maximum knock is reached. If this method is used for determinations of octane numbers on small samples, the period

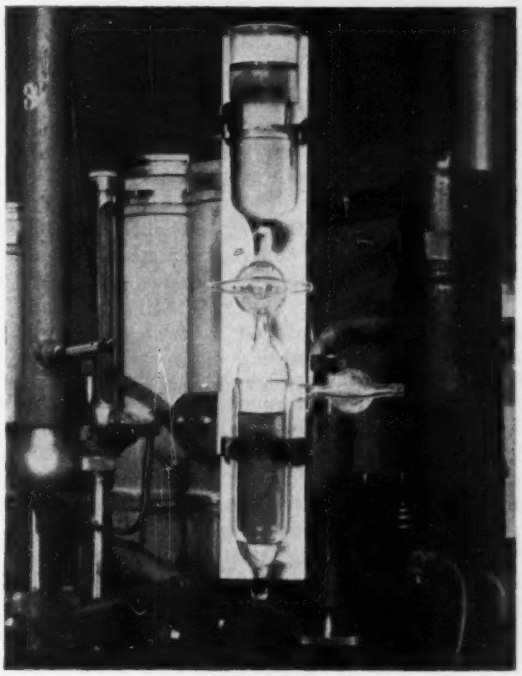


FIG 2

of time involved is unnecessarily long, and is entirely dependent upon the operator's technique in varying the air/fuel ratio. The equipment and procedure described below achieves a saving in fuel, both in the quantity held up in the float chamber and during the changeover period.

The glass unit (Fig 1) is fixed to one bowl of a standard CFR carburettor (Fig 2) and consists of an upper fuel reservoir connected to a level control chamber by means of a ground glass cock. The level control chamber has an inner reservoir, with an orifice at the bottom ground to an angle of approximately 30° to the horizontal, to provide a " chicken feed " device for maintaining a constant head of fuel. An outer

* MS received 8 February 1958.

† The British Petroleum Co. Ltd.

chamber, or annulus, completely surrounds the inner reservoir and is fused to its top; a ground glass cock fitted at the top of the outer chamber provides a means of controlling the admission of air to the apparatus. The layout of the standard fuel system is modified in that a special jet, fitted in place of the standard horizontal jet, isolates the sight glass from the fuel line as

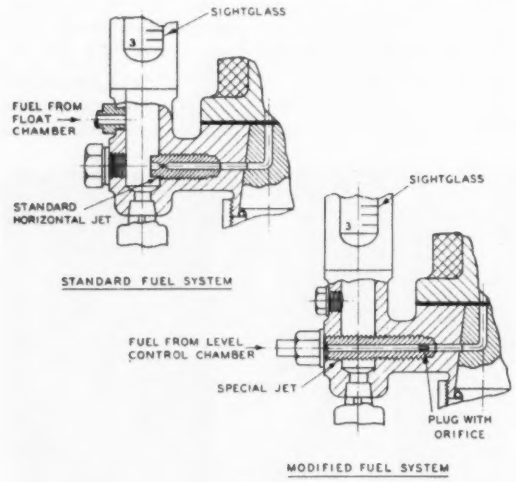


FIG 3

shown in Fig 3. The level control chamber is connected to the jet with $\frac{1}{8}$-inch bore PVC hose, and a T-junction is provided in its length for draining the system. The standard carburettor bowl adjusting screw is used for altering the air/fuel ratio manually by changing the head of fuel above the horizontal metering jet. A pointer fixed to the apparatus indicates on the normal sight glass the position at which the apparatus will maintain a constant head of fuel. When a sample is poured into the upper fuel reservoir, with the interconnecting cock open, the fuel fills the system and rises in the inner reservoir. Providing the air supply to the level control chamber is shut off, the fuel level in the annulus will not rise above the orifice level. Before opening the cock to atmosphere, the interconnecting cock must be closed and with the apparatus ready for use, *i.e.* air admission cock open, careful adjustment of the interconnecting cock will allow the fuel in the annulus to rise to any desired level. If fuel is then used from the apparatus the level in the annulus will fall, progressively weakening the mixture strength, until the constant level control due to the " chicken feed " device is reached. This characteristic is employed when a predetermined quantity of fuel is required to stabilize the engine during a change-over from reference fuel.

The test procedure is based on the Standard Method in that the normal carburettor bowls are used for reference fuels. The approximate octane number of the test fuel is found in the usual way and its air/fuel ratio position for maximum knock determined by manual adjustment of the apparatus using the chicken feed to control fuel level. This maximum knock position is noted, as a reading on the sight glass scale, and all subsequent readings for maximum knock on the test fuel are obtained by a method entailing very little manual air/fuel ratio adjustment. While the engine is running on a reference fuel, the air/fuel ratio of the test fuel is enriched manually until the fuel level is 0·2 inch above its position for maximum knock. When the carburettor selector valve is set so that the engine draws fuel from the apparatus, the quantity of fuel, pre-set in the annulus by the method described above, will be just sufficient for stabilization of the engine, the air/fuel ratio being weakened as the fuel level in the annulus drops. When level control commences at orifice level, the fuel head is constant at 0·2 inch above maximum knock and the remainder of the adjustment is made manually. By this means a fixed quantity of fuel is consumed in stabilizing knock and the manual adjustment required for accuracy of rating is retained.

Using this equipment, it is possible to determine the octane number, under Motor Method conditions, of 60 ml samples of sensitive fuels with an accuracy comparable to that of the Standard Method. Further, this method shows a saving of fuel over the published small sample method using the small float bowl fuel system, which requires between 75 and 100 ml of fuel.

ACKNOWLEDGMENT

The author wishes to thank the Chairman and Directors of The British Petroleum Company Ltd. for permission to publish this article, which is based on work carried out at the BP Research Station at Sunbury-on-Thames.

References

[1] ASTM Motor Method D.357 and Research Method D.908.
[2] " ASTM Standards on Petroleum Products and Lubricants," 1951, Appendix VI.

A NOTE ON COLOUR FORMATION WITH *PARA* PHENYLENE DIAMINE INHIBITORS*

By GEO. E. MAPSTONE‡ (Fellow) and A. HAY†

SUMMARY

N.N.′ Di-*sec* butyl *para* phenylene diamine was shown to develop colours with phenols. It is suggested that the colour development is due to the formation of an indophenol.

INTRODUCTION

THE use of oxidation inhibitors in gasoline to improve storage stability is virtually universal. The great variety of inhibitors commercially available is largely due to the fact that the requirements and effectiveness of different inhibitors differ from one application to the next.

The diamino benzene type inhibitors have found much favour where the inhibited gasoline is subsequently washed with alkaline solutions, as they are not extracted. However, their use is sometimes followed by the development of a purple colour in the gasoline, which has been generally attributed to the presence of phenols. This communication presents data which fully confirm this, and also a hypothesis to explain the colour development.

TABLE I

Colours Developed on Exposure of Solution to Sunlight
(4 cm cell)

Compound	Class *	Colour		
		Blue	Red	Yellow
Salicylic acid	P	7	7	3
Thiophenol	P	0	7	7
Mixed cresols	P	0	11	6
Mixed xylenols	P	0	11	6
Phenol	P	0	10	6
o Cresol	P	0	6	3
m Cresol	P	0	10	3
B Naphthol	O	0	1	3
Phenol phthalein	O	0	1½	1
Hydroquinone	O	0	3	2
N Monobenzyl *p* amino phenol	O	0	1	2
N Methyl *p* amino phenol	O	0	5	4
2 : 4 Di methyl 6 *t*-butyl phenol	B	0	7	3
2 Methyl 4 : 6 di *t*-butyl phenol	B	0	5	3
Pentachlor phenol	B	1·2	5	0
Aniline	M	0	3	3

* P = Para position to hydroxyl groups free.
O = Position para to hydroxyl group blocked but at least one ortho position free.
B = All ortho and para positions blocked.
M = Miscellaneous.

EXPERIMENTAL

N.N.′ Di-*sec* butyl *para* phenylene diamine (I) was selected as the amine-type inhibitor as it is very extensively used. Solutions in 80 : 20 *iso*octane-*n* heptane (reference fuel grade) containing 0·1 per cent by weight of different materials were prepared. Ten ml of each of these solutions were mixed with 10 ml of 0·1 per cent solution of (I) in the same solvent and allowed to stand in direct sunlight (Rand) for 1½ hours. Next day the colours were determined by Lovibond tintometer (IP 17/52). The initial blends were essentially of zero colour in all cases.

The colour increases in Lovibond units are given in Table I.

Further exposure of the blends resulted in an increased blueness of the samples, most of which finally deposited a purple sediment after several months.

EFFECT OF PHENOL SUBSTITUTION ON COLOUR

Statistical examination of the colour increases for each of the groups of phenolic materials, namely, those with a free para position, those with a blocked para position but a free ortho position, and those in which all the ortho and para positions were blocked, showed that the structure of the phenol had a significant effect on the colour development.

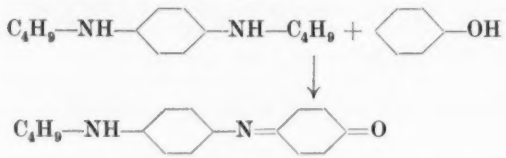
Thus, the presence of a free para position (group P) caused a statistically significant increase in both the red and yellow colours when compared with para substituted phenols (groups O and B) the increases being significant at the 1 per cent level. Comparison of groups O and B showed that the presence of a free ortho position when the para position was occupied had an inhibitory effect on the development of the red colour (significant at the 5 per cent level) but had no influence on the yellow colour.

DISCUSSION

The fact that colour development is promoted by the availability of a free para position in the phenol

* MS received 10 March 1958.
† South African Torbanite Mining and Refining Co. Ltd.
‡ Present address: Dermacult (S.A.) Pty Ltd, Box 726, Johannesburg.

suggests that the colour formation may be due to the formation of an indophenol thus:



This reaction involves both oxidation and dealkylation of the amino group. However, since the solution was saturated with air, and sunlight contains high energy radiation, this hypothesis appears to be quite reasonable. The fact that the blue colours of all the samples developed on further standing also supports this suggestion.

The inhibiting action for the development of the red colour of a free ortho position when the para position is occupied can be explained by reaction of the phenylene diamine at that position. In the absence of a reactive free position in either the ortho or para position photochemical dealkylation of the phenol or some other reaction could then allow the formation of the indophenol.

In conclusion, the hypothesis proposed to explain the colour formation is that an oxidative condensation of the phenylene diamine and a phenol takes place. In order of decreasing probability the condensation will be effected at:

(1) a free para position (to give an indophenol);
(2) a free ortho position (only slight colour);
(3) a blocked para position after desubstitution.

It is appreciated that the evidence put forward does not prove this hypothesis, but at least it does provide an explanation for the development of the colours observed.

ACKNOWLEDGMENT

The authors wish to acknowledge with thanks the permission granted by the management of the South African Torbanite Mining and Refining Company Ltd for permission to publish this note.

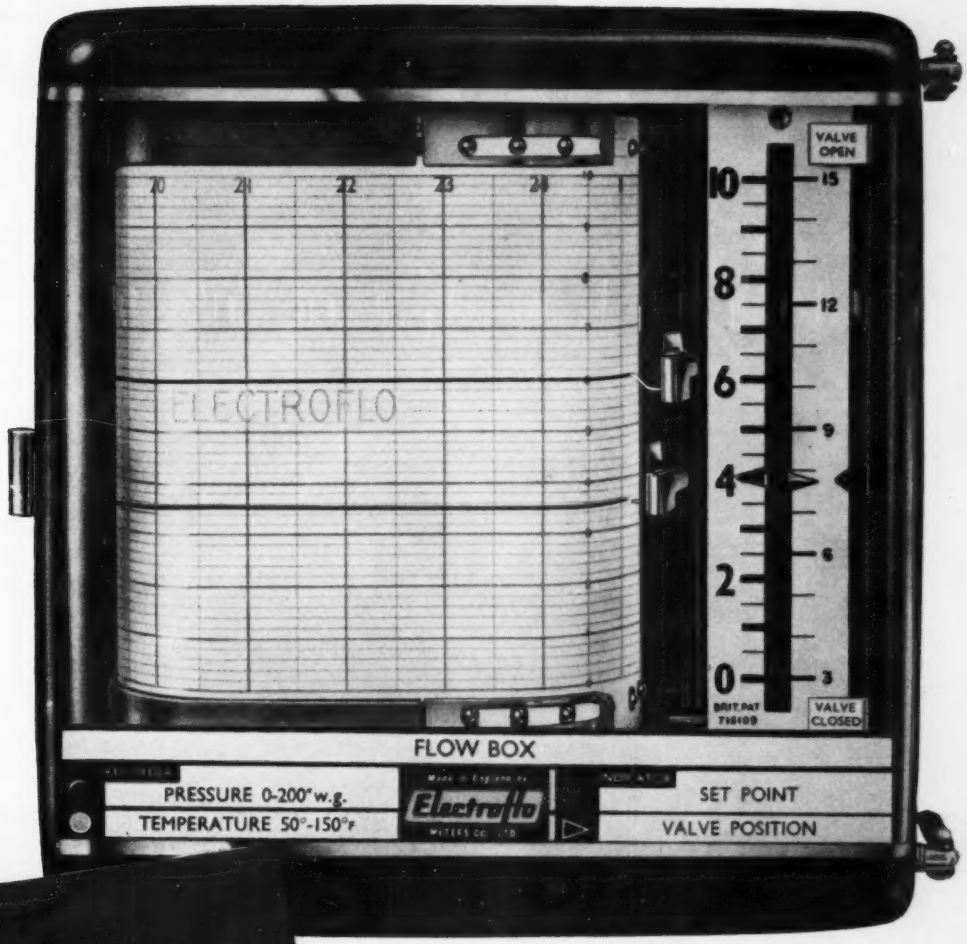
OBITUARY

DARAB FROOZANI

1919–1958

THE sudden death occurred on 17 April 1958 in Abadan, South Iran, of Darab Froozani, who had been an Associate Fellow of the Institute since 1948. He was born in Shiraz, Iran, in 1919, and graduated from the Abadan Technical Institute with a B.Sc. in petroleum technology in 1946. He was subsequently employed in the laboratory, process engineering, and safety departments of the Abadan refinery, and was a member of the Association of Iranian Engineers. Some months earlier he and Mrs Froozani had been on long leave to the U.K., where he visited the headquarters of the Institute. He had a pleasing personality and all who knew him will have pleasant memories of his friendship. He leaves a widow and a daughter of five years old.

P. J.



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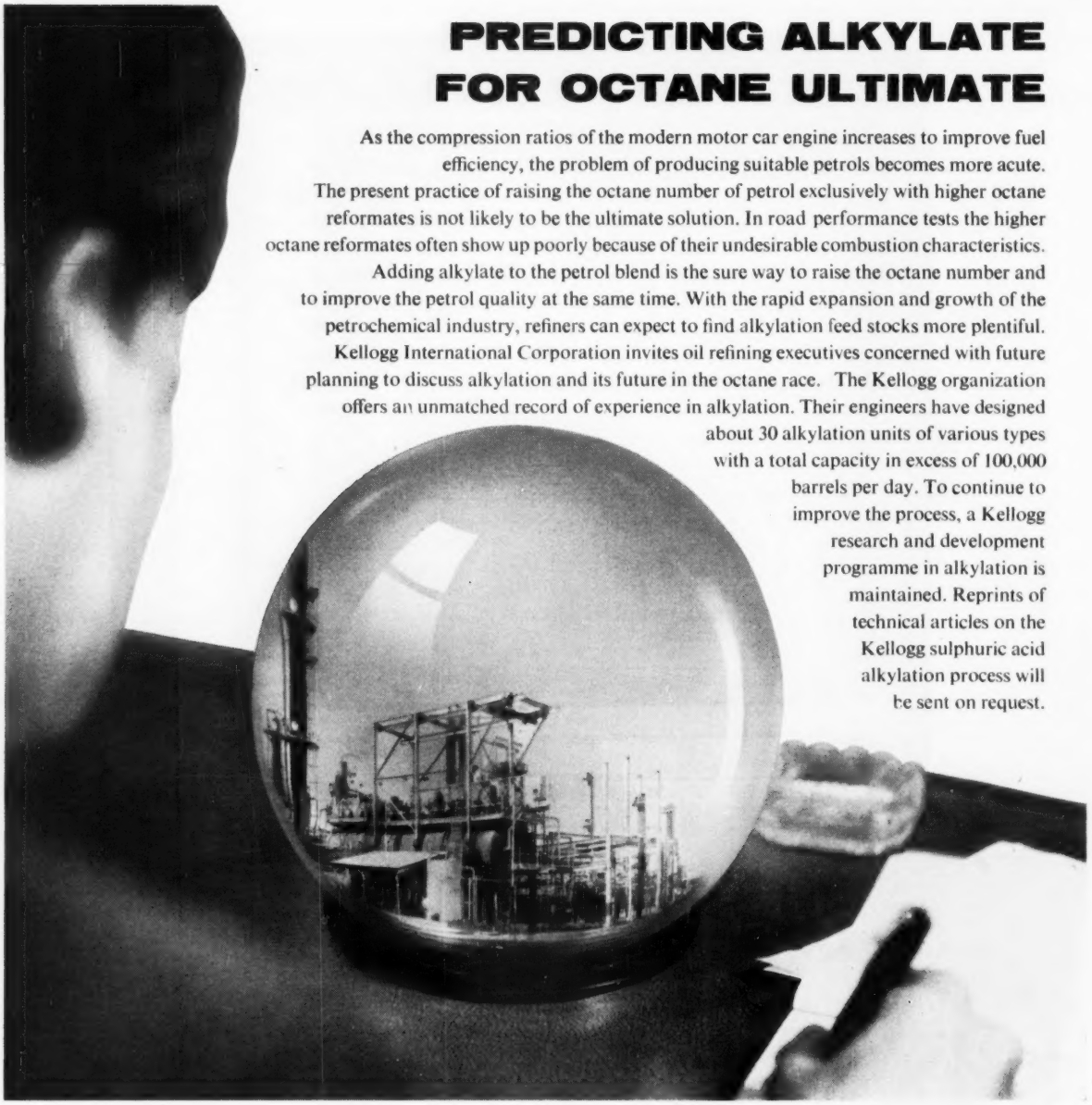

PREDICTING ALKYLATE FOR OCTANE ULTIMATE

As the compression ratios of the modern motor car engine increases to improve fuel efficiency, the problem of producing suitable petrols becomes more acute. The present practice of raising the octane number of petrol exclusively with higher octane reformates is not likely to be the ultimate solution. In road performance tests the higher octane reformates often show up poorly because of their undesirable combustion characteristics. Adding alkylate to the petrol blend is the sure way to raise the octane number and to improve the petrol quality at the same time. With the rapid expansion and growth of the petrochemical industry, refiners can expect to find alkylation feed stocks more plentiful. Kellogg International Corporation invites oil refining executives concerned with future planning to discuss alkylation and its future in the octane race. The Kellogg organization offers an unmatched record of experience in alkylation. Their engineers have designed about 30 alkylation units of various types with a total capacity in excess of 100,000 barrels per day. To continue to improve the process, a Kellogg research and development programme in alkylation is maintained. Reprints of technical articles on the Kellogg sulphuric acid alkylation process will be sent on request.

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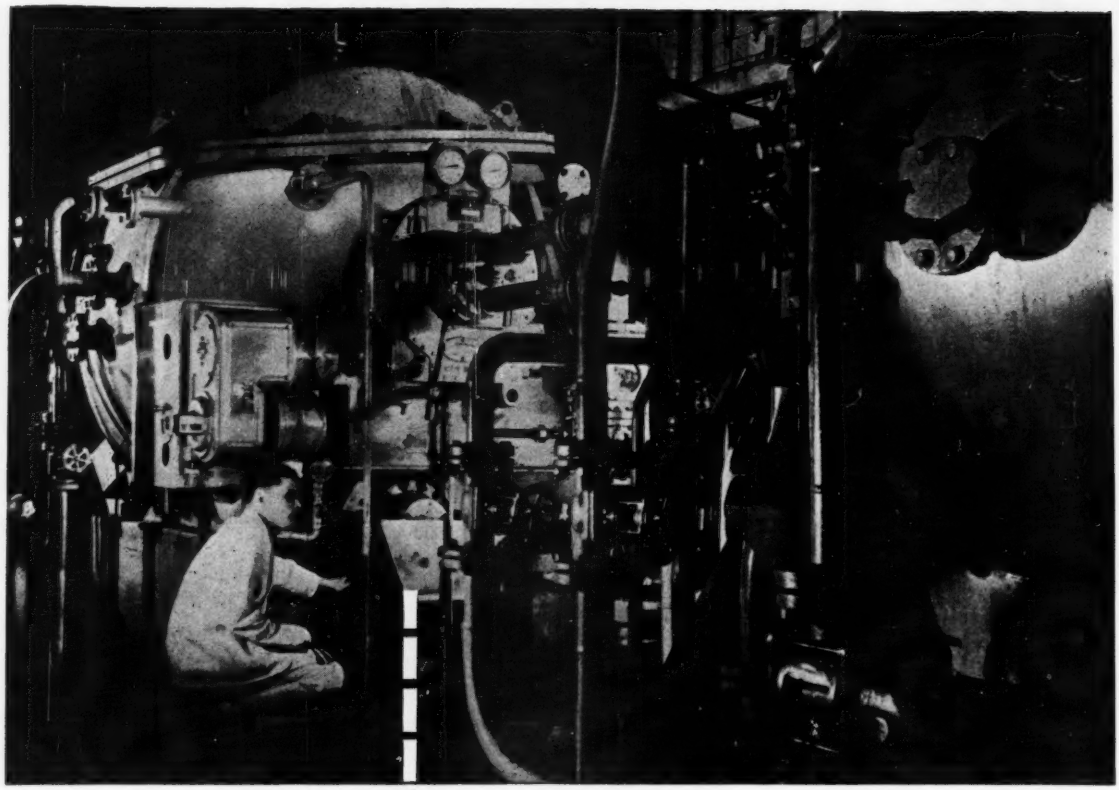

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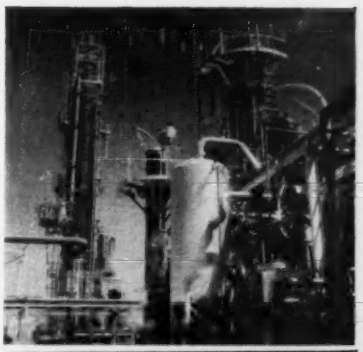
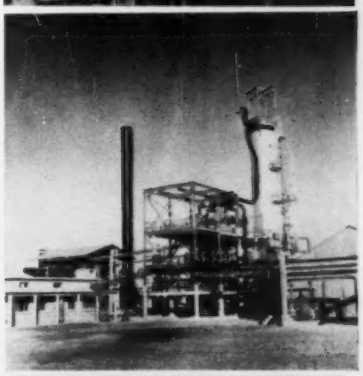


Propane Deasphalting Unit and Vacuum Distillation Unit.

IRAQ

Left
Crude Oil Stabilization Unit at Kirkuk. For the Iraq Petroleum Co.

Right
Crude Oil Distillation Unit at K1 Pump Station.



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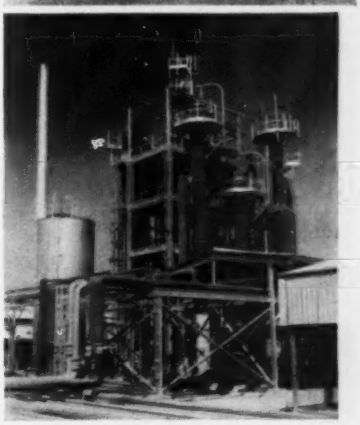

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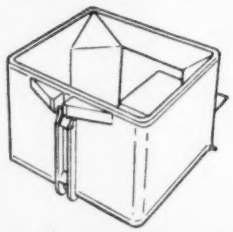
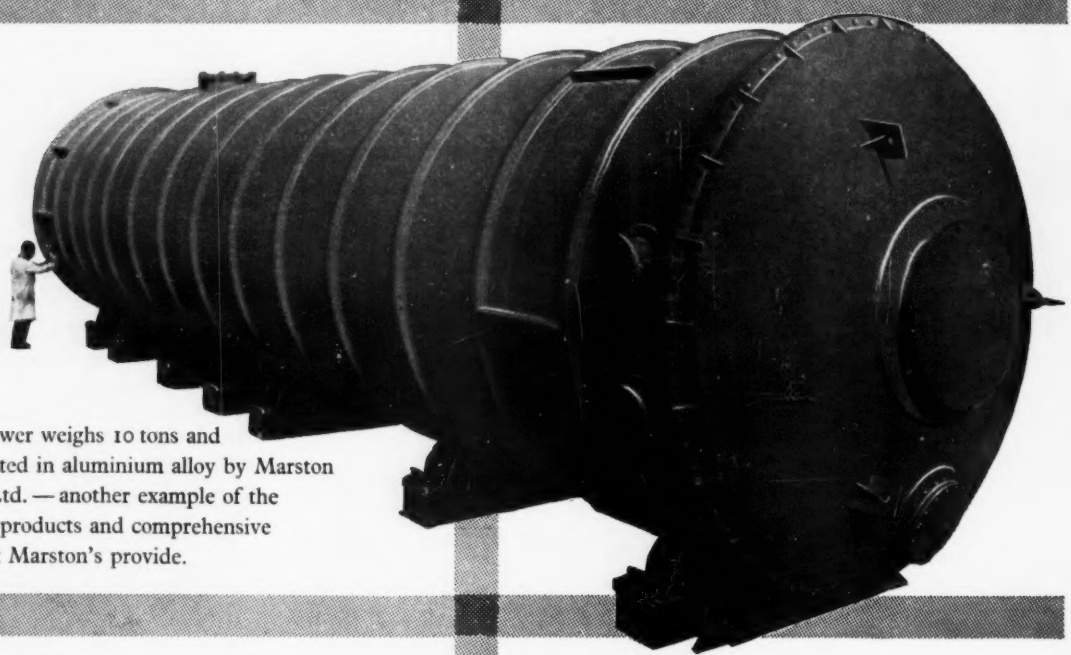
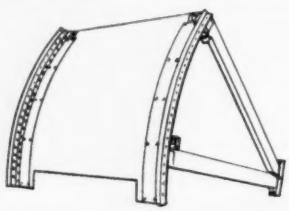


This truck-container is designed to carry granular material of particle size approximately $\frac{1}{16}$″. Special attention had to be paid to the fit of the door and the smooth finish of the interior. The body ($\frac{3}{8}$″ plate 'Kynal' M 39/2) was welded by the Argon arc and Argonaut processes.



This 52′ tower weighs 10 tons and was fabricated in aluminium alloy by Marston Excelsior Ltd. — another example of the specialised products and comprehensive service that Marston's provide.



This radial sluice-gate is 6′ 6″ wide and 6′ high. It is made of aluminium alloy, to minimise maintenance costs. To obtain a clean design free from any crevices where corrosion might start, the gate was welded by the Argon arc process. It is believed to be one of the first examples in this country of a radial sluice-gate in welded aluminium alloy.

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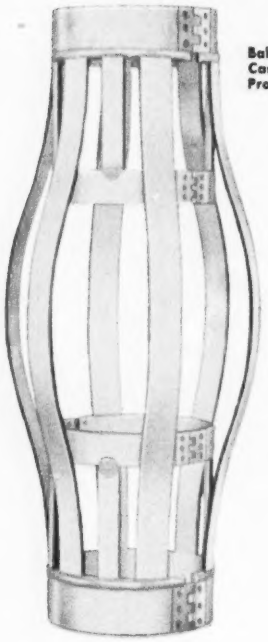


Baker Model "H-20"
Casing Centralizer
Product No. 9112

a size and type...

Model "H-50"
(5" Bowed Height)
Product No. 9114

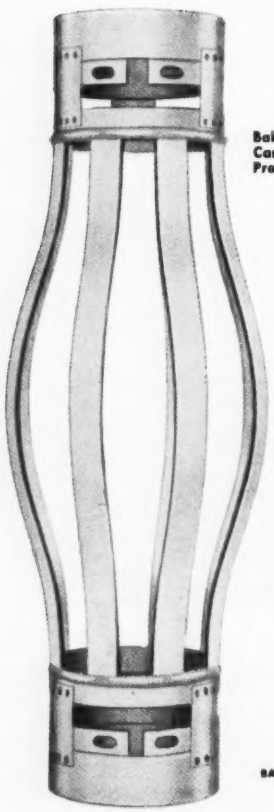
Model "H-25"
(2½" Bowed Height)
Product No. 9113

Model "H-15"
(1½" Bowed Height)
Product No. 9115

Model "H-20"
(2" Bowed Height)
Product No. 9112

"TAILORED" to your needs because Baker Casing Centralizers are made with bowed height ("effective reach") of springs from 1¼" to 5"—for a range of open hole diameters from 5⅜" to 26½"—and to run on casing sizes from 4½" to 16". It's easy to see that the *exact* size is available to fit *your* casing and provide effective centering in the greatest practical range of open hole diameters.

"tailored" to your needs...



Baker Model "G-20"
Casing Centralizer
Product No. 910-G

Model "G-20"
(2" Bowed Height)
Product No. 910-G

Model "G-12"
(1¼" Bowed Height)
Product No. 910-G

Model "G-15"
(1½" Bowed Height)
Product No. 910-G

"TAILORED" to your wishes, and you can choose between the Baker Model "H" HINGE-LOK Centralizer which is closed and locked around the casing coupling or stop ring—or you may prefer the Baker Model "G" SLIP-ON Centralizer which is merely slipped over the casing and positioned with stop rings.
Ask the Baker representative about "Protective" primary cementing using Baker Casing Centralizers in combination with Baker Wall Scratchers and Baker Cementing Shoes and Collars.

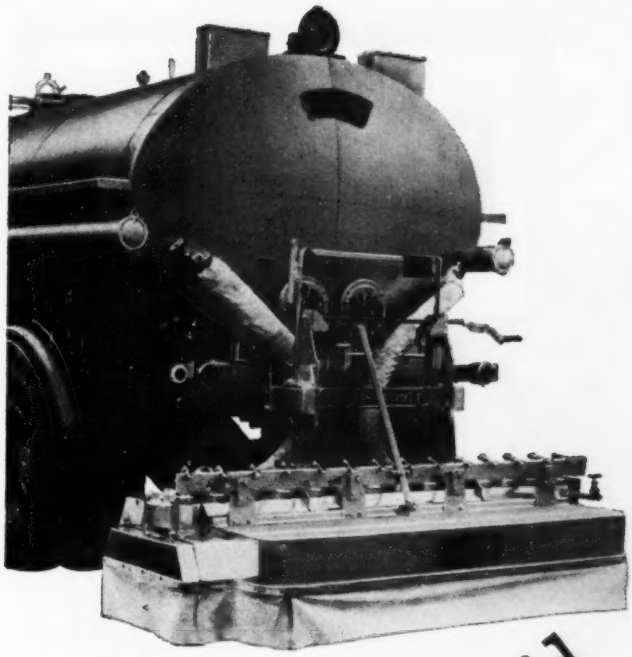
for better cementing

One of the partners in
BAKER "Protective" Cementing

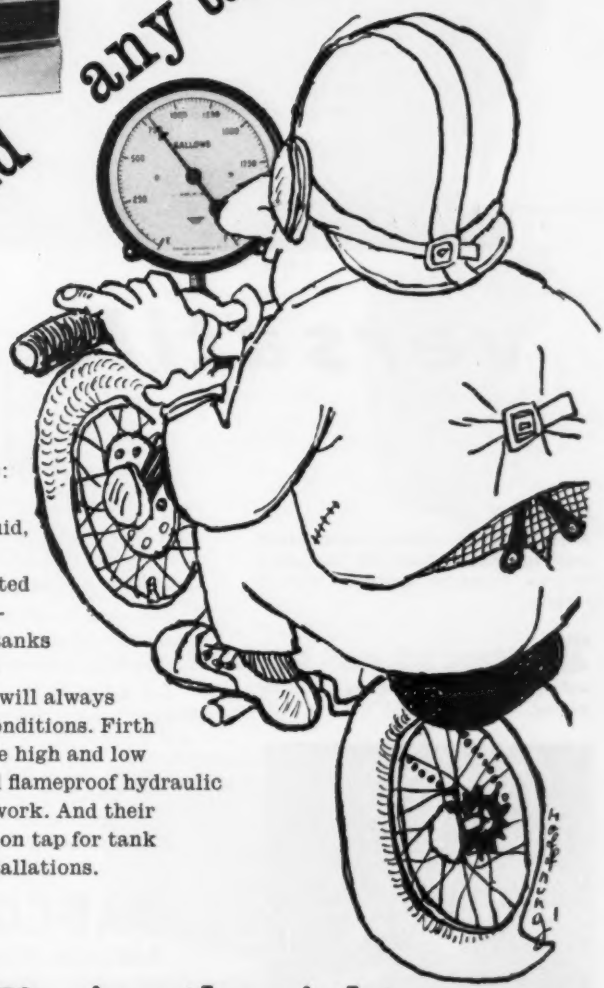
Baker Flexiflow Fill-Up Collars and Shoes
Baker Casing Centralizers
Baker Wall Scratchers

BAKER
CASING CENTRALIZERS

BAKER OIL TOOLS, INC. HOUSTON • LOS ANGELES • NEW YORK



any liquid any tank anywhere



The long and the short of it is this: if you need a regular quick check on the head, weight or volume of any liquid, you need a Firth Cleveland Contents Gauge. The indicator can be mounted on the tank—any kind of tank—or hundreds of feet away. Several tanks can be checked from a single indicator, and the measurement will always be accurate—whatever the conditions. Firth Cleveland also provide high and low level warning devices and flameproof hydraulic gauges for control work. And their technicians are always on tap for tank calibrations and gauge installations.

FIRTH CLEVELAND CONTENTS GAUGES give the right answer

Manufactured by: **FIRTH CLEVELAND INSTRUMENTS LTD.** (A subsidiary of Simmonds Aerocessories Ltd.)

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Head Office & Works: Treforest, Pontypridd, Glamorgan. **A member of the Firth Cleveland Group.**

FC

CRC240

BABCOCK

versatile FUSION WELDING

Bottom Right
A Babcock fusion-welded treating tower prior to despatch from the Company's Renfrew Works, for installation at an oil refinery.

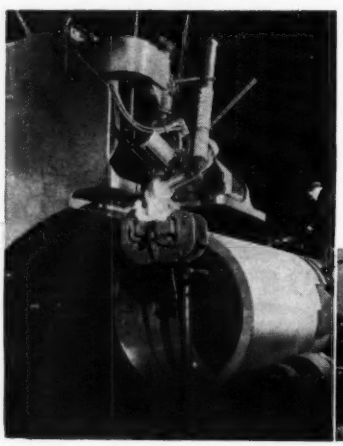
Below
Automatic fusion-welding of a thick-walled pressure vessel at Renfrew Works.

The 75 ft.-long by 10 ft.-diameter pressure vessel shown above during installation at the Patchway Works of Bristol Aero-Engines Limited, is part of a special test cell nearly 90 ft. long fabricated by Babcock & Wilcox Ltd. in molybdenum steel, by the *BABCOCK fusion-welding process.*

Designed for the testing of ramjet and turbojet engines, this impressive test plant reproduces simultaneously the conditions of high air speed and low atmospheric pressures associated with high-altitude and supersonic flight.

So, BABCOCK fusion-welding, with its fine reputation in the construction of many hundreds of pressure vessels for oil refineries, chemical plants and nuclear power stations, has entered the aircraft industry.

What better example of its *versatility*—in providing for *any* industry, pressure vessels up to the largest sizes and highest specifications, backed by unrivalled design, research and manufacturing facilities, and 25 years of fusion-welding experience.



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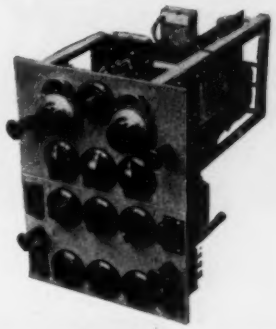
Shorts **General Purpose Analogue Computor**

The extended range of non-linear computing units now available increases the versatility of the compact Short Computor. Write for Data Sheets on these units.

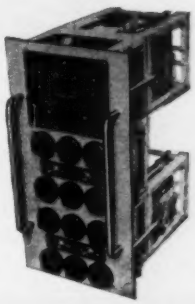
variable time switch unit

This unit permits the solution of problems in which the coefficients are changed from one discrete value to another, either after a given time or when a variable reaches a predetermined value during the period of computation.
The unit will therefore find application to problems in which a simulation is required of transient performance under abruptly changing conditions, or to problems involving integration between two limits.



servo multiplier unit

This unit supplements the HIGH SPEED MULTIPLIER UNIT. It permits four separate variables to be multiplied by one common variable.



NEW! another outstanding instrument from the same team

the low-frequency decade oscillator

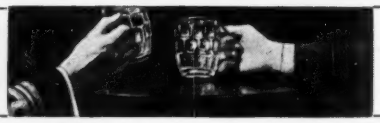
This oscillator has been designed for testing servo-mechanisms and electrical systems where inputs of extremely low distortion and accurate amplitude are essential. It employs three drift-corrected computing-type amplifiers to generate a sinusoidal oscillation in the range 0.01 to 110 c/s, according to the setting of the 3-decade frequency control. "Step" and "Ramp" functions may also be generated, and the total distortion is less than 0.5%.

All enquiries to: Short Brothers & Harland Ltd., Computor Sales Department, 208a Regent Street, W.1. REGent 8716

I'm fed up with filters!
let's sit down...

Let's sit down and talk about cricket, the weather... anything so long as it isn't your confounded Simmonds Fram Separators.

Sorry old man . . . didn't mean to bore you.



That's quite all right. Delighted to know the R.A.F. is getting up to date. So you actually fly your planes on kerosine now instead of water!

Very comical! Anyway, it's not the whole point. I admit the main object of Simmonds Fram Separators is to remove all the water, but they also take out the solids.

Little strips of erk, for instance?

. . . Anything down to 5 microns.

That gives me a big kick.
Which is more than I can say for this brew . . .

There you are. Now if we could persuade Sally to fit Simmonds Water Separators to the barrels . . .

the point of the argument... **FRAM SEPARATOR FILTERS** for clean water-free fuel

For more details of this and other Simmonds products for the aviation industry **SEND FOR LITERATURE** *to*

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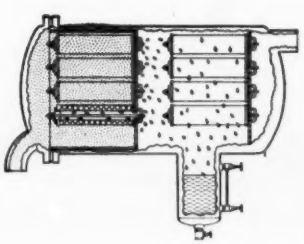
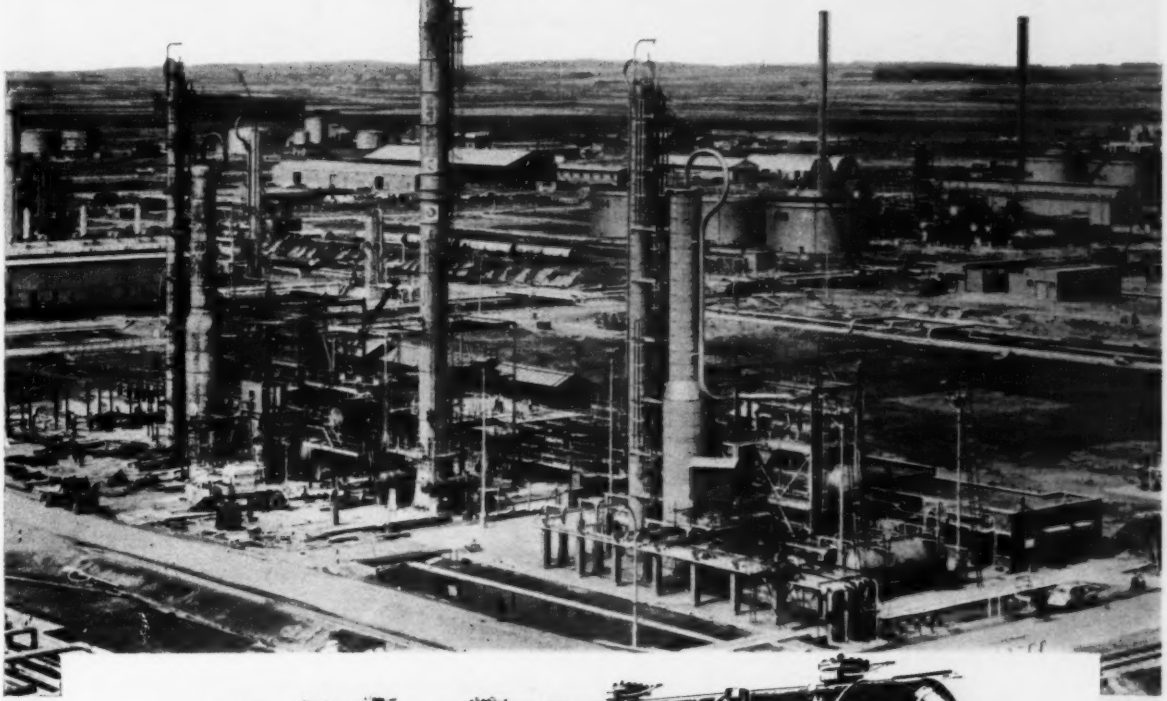


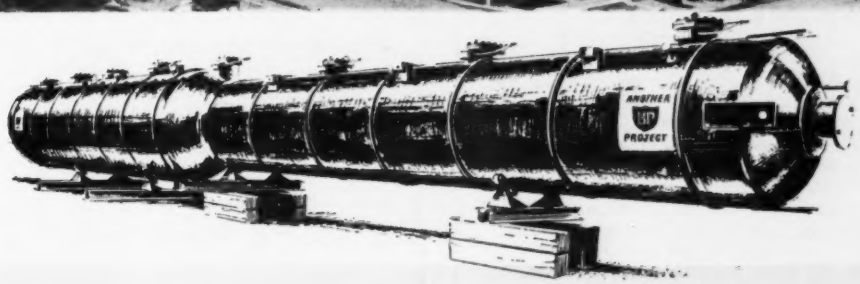
CRC 5WS

PETROLEUM PLANT

The right and left units are nos. 1 and 2 stabiliser plants, on either side of the isopentane unit, engineered and supplied for the B P Refinery (Kent) Ltd. B P design. Here also Power-Gas jointly with W. J. Fraser & Co. Ltd. were responsible for the installation of offsite and general services for the refinery extensions.

Engineering, manufacture, procurement, site construction and management are available to suit the particular requirements of the project—a comprehensive service to meet the specialised requirements of the Petroleum Industry for new sites, replacement or extension.





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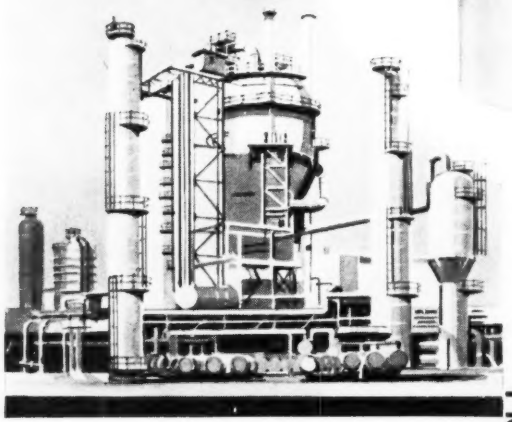
MILLENNIUM KEY



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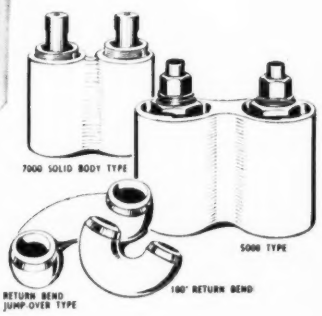
highest quality fittings for refinery and chemical plants



Please write for bulletins which give full technical information on each type of fitting.

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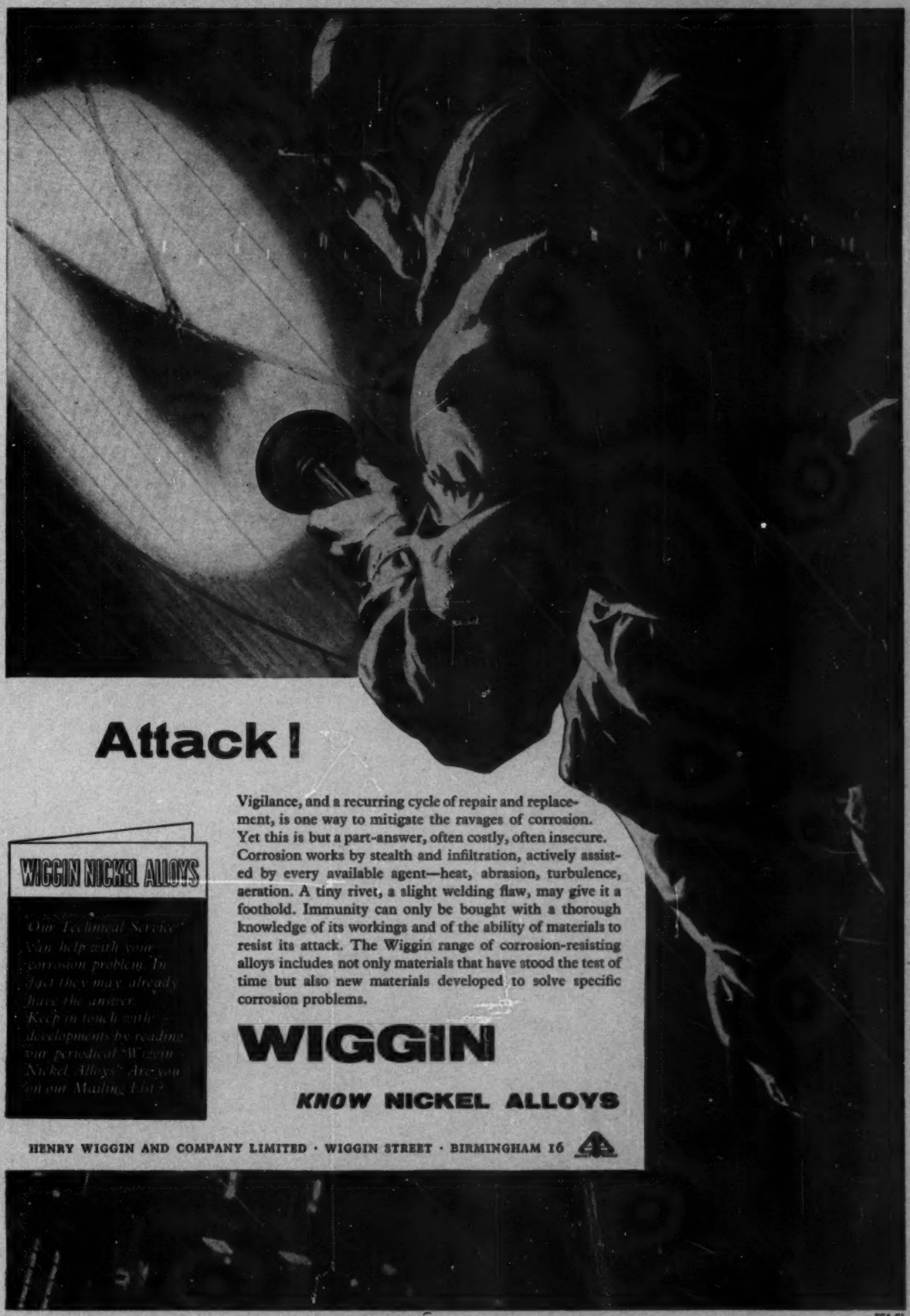

Attack!

Vigilance, and a recurring cycle of repair and replacement, is one way to mitigate the ravages of corrosion. Yet this is but a part-answer, often costly, often insecure. Corrosion works by stealth and infiltration, actively assisted by every available agent—heat, abrasion, turbulence, aeration. A tiny rivet, a slight welding flaw, may give it a foothold. Immunity can only be bought with a thorough knowledge of its workings and of the ability of materials to resist its attack. The Wiggin range of corrosion-resisting alloys includes not only materials that have stood the test of time but also new materials developed to solve specific corrosion problems.

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